Pollution Control Services Department
101 S. Richey, Suite H
Pasadena, Texas 77506
FAX: 713-274-6475
713-920-2831

RECEIVED
17 JAN 17 PM 2:22
SUPERFUND DIV.
REMEDIAL BRANCH
(6SF-R)

January 12, 2017

VIA CERTIFIED MAIL 7016 0340 0000 8302 8903, RETURN RECEIPT REQUESTED, AND
VIA ONLINE SUBMISSION AT www.epa.gov/tx/forms/sjrwp-comments

Mr. Gary Miller
Remedial Project Manager
Region 6 (6SF-RA)
United States Environmental Protection Agency
1445 Ross Avenue
Dallas, Texas 75202-2733

Subject: Comments on Proposed EPA Cleanup Plan for the San Jacinto River Waste Pits Superfund Site (the Proposed Cleanup Plan)

Dear Mr. Miller:

The Harris County Technical Review Team (Harris County TRT) would like to thank the EPA for selecting alternative 6N and 4S (removal – northern and southern impoundments) as the preferred remedy for the San Jacinto River Waste Pits Superfund Site (hereinafter referred to as the Dioxin Pits). The Harris County TRT wishes to ensure that in the future, the health of all of its residents and the environment is protected from the Dioxin Pits.

As the EPA described in the Proposed Cleanup Plan, the temporary armored cap has had numerous "instances of erosion or missing armor stone" and has "required many repairs and extensive maintenance."[1] In fact, additional maintenance has been required since the issuance of the Proposed Cleanup Plan. The need for routine unplanned repairs illustrate the difficulties and challenges in constructing a reliable permanent cap at the Dioxin Pits. Even with the upgrades proposed for Alternative 3N, the reliability of the cap is highly questionable. The configuration of the channel at this Site, storm surge,[2] the presence of the Interstate 10 Bridge and the active tug and barge operations make prediction of currents, waves and erosion complex, which adds a high level of uncertainty to the results. Given the Site conditions and past performance of the temporary cap (which was designed and installed by the PRPs), the Harris County TRT believes it is impossible to design and construct a permanent cap at this Site that will be reliable for hundreds of years. Additionally, it is uncertain that the PRPs will continue to operate and remain fiscally sound for hundreds of years to conduct maintenance activities, surveys and repairs over this extended time. Therefore, the Harris County TRT supports EPA's selection of Alternative 6N and 4S and submits the following comments and recommendations to the EPA regarding the Proposed Cleanup Plan.

9793774

[1] Proposed Cleanup Plan, Site History, Page 4.
[2] While it is not the only threat to the Dioxin Pits, the Harris County TRT believes that storm surge is one of the most ominous threats.

I. Cleanup Level Should Be More Protective – The Primary Remediation Goal Should Consider Subsistence Fishing

The Proposed Cleanup Plan utilized a recreational fisher receptor to develop its Primary Remediation Goal (PRG) for the Dioxin Pits. The EPA based this decision on a 2013 Texas Department of State and Health Services (DSHS) risk assessment that "could not identify subsistence fishers in the area" of the Dioxin Pits.[3] For the reasons set forth below, the Harris County TRT urges the EPA to include subsistence fishers in development of the PRG for the Dioxin Pits. To do otherwise potentially exposes residents to unacceptable levels of dioxin.

The EPA defines subsistence fishers as "fishers who rely on non-commercially caught fish and shellfish as a major source of protein in their diets." (USEPA, 2000). Importantly, EPA guidance documents note that "there is often not a clear distinction between sport and subsistence fishers. Many individuals would not consider themselves subsistence fishers but do rely on non-commercially caught fish for a substantial portion of their diet." (USEPA, 2000). It follows that "[u]nless surveyed specifically, subsistence fishers may be under-represented by available surveys."[4]

The EPA's own policies assume that subsistence fishers constitute 10% of the licensed fishing population in an area. (USEPA, 2004). The 2013 DSHS assessment itself noted that subsistence fishing, while not documented in this waterbody, likely occurs. They also assumed that subsistence fishers constitute 10% of the licensed fishers in assessing risks of seafood consumption, which is in keeping with the aforementioned EPA policy.

Additionally, given the socioeconomic conditions and diverse demographic characteristics of persons residing near the Site, it would be more reasonable to assume that subsistence fishers do exist. The 2011 National Survey of Fishing, Hunting, and Wildlife-Associated Recreation (USDOI *et al.*, 2014) highlights the importance of urban residents in fishing, with two-thirds of Texas anglers residing in metropolitan statistical areas with populations exceeding 1 million: Dallas-Fort Worth-Arlington; Houston-Sugarland-Baytown; San Antonio; and Austin-Round Rock. Approximately 20% of Texas anglers reported household incomes of less than $20,000. Among fishers surveyed by the Texas Parks and Wildlife Department in Galveston Bay in 1981 during the black drum run, the average number of days spent fishing per year was 63, and 20% responded that obtaining fish for eating was extremely important to them. (Dutton *et al.*, 1988). Thirty percent of those fishers reported a mean household income under $20,000.

The Texas Parks and Wildlife Department game warden in charge of patrolling the San Jacinto River, including the Dioxin Pits, is in the best position to assess subsistence fishing in that area. The game warden stated in a sworn affidavit that "the biggest users of the River near the Dioxin Pits are the bank fishermen and it is clear that many of them are subsistence fishing and use the fish they catch to feed their families." The game warden also notes the difficulties in enforcing fishing regulations at the Dioxin Pits with existing staffing levels. This affidavit, and those of a number of subsistence fishers, are included in the administrative record as attachments to document 100001100.[5]

---

[3] Proposed Cleanup Plan, Remedial Action Objectives and Preliminary Remediation Goals, Page 19.
[4] *Id*
[5] Letter from Harris County Attorney Vince Ryan and Managing Attorney Rock Owens to Suzanne Murray, dated January 15, 2013.

Based on this evidence and current EPA policies, we urge the EPA to consider subsistence fishing to be an existing use at the Site, and to set PRGs that are protective of this use.

II. Cleanup Level Should Be More Protective – Biota-Sediment Accumulation Factor

We request that the best available science and information be applied in developing the Proposed Cleanup Plan. Specifically, the Harris County TRT requests that the EPA use a more accurate, site-specific biota-sediment accumulation factor (BSAF) that is supported by available site and species specific data. BSAF is a key parameter relating contaminant concentrations in fish to those in sediment. Since fish consumption is the primary source of site-derived risk, the BSAF strongly influences the sediment PRG. An accurate BSAF and conservative risk assumptions ensure that the residual risk from the Site to fish consumers is minimized.

A tremendous amount of data has been collected locally over the past 15 years to enable quantification of BSAFs for dioxins in the key species of concern. Much of it was funded by the TCEQ and EPA and performed according to EPA recommendations for the development of BSAFs, EPA methods, and EPA-approved quality assurance project plans (QAPP). BSAFs for the Site have also been published in peer-reviewed scientific literature cited below.

As described in the August 29, 2016 memorandum "Human Health Risk Evaluation and Recommended Sediment Cleanup Level for Site Specific Exposure to Sediment at the San Jacinto River Superfund Site" from Ghassan A. Khoury to Gary Miller,[6] the sediment PRG was calculated largely on the basis of a fish tissue target of 3.13 ng/Kg in fish tissue divided by a BSAF of 0.09. After inclusion of risks due to shellfish consumption, sediment incidental ingestion, and dermal exposure, the PRG for dioxin Toxic Equivalent Quotient (TEQ) was rounded to a single significant digit at 30 ng/Kg. The BSAF used in the calculation was a default value from a national study that is neither specific to the Site nor the species. This would be appropriate only if there were no other data available from the Site or species of interest.

We believe that the default BSAF underestimates the actual bioaccumulation for the species of interest (hardhead catfish) in this system, and results in under-protection of the fish consumption use. We recommend that the EPA either re-calculate the BSAF according to EPA-recommended methods (Burkhard, 2009) using the best and most appropriate available data, or that they adopt a value of 0.39, the median BSAF for 2,3,7,8-TCDD in the San Jacinto River/Houston Ship Channel System for hardhead catfish. (Dean *et al.*, 2009).

The available data sources to calculate a site-specific dioxin BSAF are extensive. They include hundreds of paired catfish, blue crab, and surface sediment samples referenced below. Additionally, there is extensive data collected by the TDSHS, TCEQ PA/SI program, and NPDES permittees, but it does not include paired sediment and tissue sampling, thus it was not utilized here.

[6] Proposed Administrative Record, Document Number 100001024.

In 2001 work for the Texas Clean Rivers Program and the Houston-Galveston Area Council, Parsons and PBS&J collected and analyzed paired catfish/sediment samples from 14 sites throughout the Houston Ship Channel system, including the San Jacinto River and Galveston Bay. Thirteen of the catfish samples were hardhead catfish. Paired blue crab/sediment samples were collected from 16 sites. All tissue samples were composites of at least three fish or crabs of harvestable size, and analyzed for 17 2,3,7,8-substituted PCDD/PCDF congeners and lipid content by EPA Method 1613. All sediment samples were composites of multiple surface sediment grabs, and analyzed for the same 17 congeners as well as organic carbon content. The data was collected in accordance with a TCEQ-approved QAPP. This data is provided in report form (PBS&J and Parsons, 2001), and is appropriate for development of a site-specific BSAF.

From 2002 to 2005, the University of Houston and Parsons collected approximately 150 paired surface sediment, blue crab, and catfish samples from the Houston Ship Channel system including the San Jacinto River under the EPA Total Maximum Daily Load (TMDL) Program. The vast majority of the catfish samples were hardhead catfish, but a substantial number of blue catfish samples were also collected and separately analyzed. All tissue samples were composites of at least three fish or crabs of harvestable size, and analyzed for 17 2,3,7,8-substituted PCDD/PCDF congeners and lipid content by EPA Method 1613. All sediment samples were composites of multiple surface sediment Ponar grabs that collected only the surface layer, and analyzed for the same 17 PCDD/PCDF congeners as well as organic carbon content. Some samples of other fish species, shrimp, and oysters were also collected and analyzed, as well as water (dissolved and suspended solids), and sediment cores. The data was collected in accordance with a TCEQ- and USEPA-approved QAPP, and the specific objectives including calculation of BSAFs to be used in TMDL development. This data is available online from the TCEQ at http://www80.tceq.texas.gov/SwqmisPublic/public/default.htm. It is also available in report form. (University of Houston and Parsons, 2013).

In 2011 and 2012, the University of Houston and Parsons collected approximately 60 additional paired catfish and surface sediment samples from the Houston Ship Channel system using the same methods and EPA-approved QAPP as the 2002-2005 study. However, no blue crabs were collected. This data is provided in a report. (University of Houston and Parsons, 2013). The EPA has thus paid for much of this data and oversaw its collection via an EPA approved QAPP.

In summary, we believe the EPA underestimated the actual BSAF and should calculate a site-specific value from available data, as in Dean *et al.*, (2009) and University of Houston and Parsons, (2013) or should use the median measured BSAF of 0.39 for hardhead catfish.

III. Cleanup Level Should Be More Protective – Sediment Preliminary Remediation Goals

The Harris County TRT researched cleanup levels for dioxins at other Superfund sites and requests the EPA order a cleanup of the Dioxin Pits that is consistent with these other sites. A summary of our findings are shown in the table attached as Exhibit A. The three most recent sites are in tidal rivers where there is fishing activity (Diamond Alkali Lower Passaic River, Portland Harbor Willamette River, and Lower Duwamish Waterway). For the Lower Passaic River the cleanup level for 2,3,7,8-TCDD is 8.3 ng/Kg. For the Willamette River, the site-wide cleanup level for 2,3,7,8-TCDD is 0.6 to 2 ng/Kg. For the Lower Duwamish River, the site-wide cleanup level for Dioxin TEQ is 2 ng/Kg in the top 10 centimeters (cm) of surface sediment and 13 to 37 ng/Kg in the top 45 cm of sediment.

Therefore, the Harris County TRT requests that EPA re-calculate the sediment PRG using the site-specific BSAF values presented above and considering subsistence fishing in the San Jacinto River. With these factors, we expect that a re-calculation of the sediment PRG would yield a value lower than the local background dioxin TEQ level of 7 ng/Kg in the San Jacinto River. Therefore, the PRG for this Site should be set at the local background level or below as ordered by the EPA at similar dioxin Superfund sites.

IV. All Sediment Exceeding the PRG Should Be Remediated

The Proposed Cleanup Plan does not provide for remedial measures to address contaminated sediment above the PRG outside of removal of the Site waste. The rationale for this is that when all surface sediments within the preliminary Site perimeter are averaged together, the average concentration does not exceed the PRG. This is concerning to the Harris County TRT because it leaves several areas where contaminants mobilized from the Dioxin Pits are present at concentrations far in excess of the dioxin PRG (including, but not limited to the Sand Separation Area, the area west of the Dioxin Pits, and the area south of the South Impoundments as shown on Figure 2-8 of the Interim Final Feasibility Study Report). We recommend that these areas be remediated. Decisions on where to remediate should not be based on the dimensions of the preliminary site perimeter, but on the extent of actual contamination.

V. Implementation of Alternative 6N and 4S – Transport and Staging of Dioxin Waste

The Proposed Cleanup Plan does not provide specific plans for transportation of the dioxin waste, disposal of the dioxin waste at an authorized waste disposal facility, or preventing and responding to the release of the dioxin waste into the environment during transit to the dewatering and stockpile staging area. According to the feasibility study, the sludge and sediment at the Site do not contain a listed hazardous waste and do not meet the characteristics of hazardous waste. It is recommended the EPA perform a thorough hazardous waste determination and classification, including a listed waste review, to ensure the dioxin waste is disposed of per the Resource Conservation and Recovery Act (RCRA), if applicable, and/or the Texas Solid Waste Disposal Act (TSWDA). Furthermore, it is recommended a waste management plan be developed that utilizes Best Management Practices (BMPs) for waste transport. The Harris County TRT requests that the following BMPs be included in the waste management plan: enclosed transportation vehicles to prevent leaks or loss of material; maintaining a contract with an entity capable of cleaning up and properly disposing of the dioxin waste in the event that a spill/release occurs; and an EPA approved formal contingency plan should a release occur during transit to the approved disposal facility.

Furthermore, the Proposed Cleanup Plan does not address the prevention and management of potential releases during the dewatering of the dioxin waste in the processing areas. The processing areas should meet the location standards required by State and Federal regulations. In order to prevent releases of dioxin waste to the environment, the dewatering area should be completely enclosed. The Harris County TRT requests that a formal contingency plan be prepared in case of a major storm event. Furthermore, a spill prevention and control plan should be in place that requires secondary containment, and that the processing area be designed to contain and prevent spills from leaving the Site. In order to prevent nuisance conditions to nearby receptors, the staging area should be isolated from residential properties and odor/dust control measures should be taken. Contaminated water or other wastes generated during the treatment process should be minimized and disposed of at an authorized facility.

VI. Implementation of Alternative 6N and 4S – Engineering and Design

The Harris County TRT agrees with EPA's recommendation that the San Jacinto River Waste Pit excavation should be performed in the dry to limit re-suspension of the dioxin-contaminated waste material during excavation and processing activities as detailed in Alternative 6N of the EPA Proposed Cleanup Plan (2016). Due to seasonal variability in the high water level of the River, we agree with EPA's recommendation to use soil and rock berms or interlocking sheet pile coffer dams to isolate the contaminated sediment site from the River for excavation. Simultaneously, the Harris County TRT agrees with EPA's recommendation to treat all project site wastewater generated during waste decant/dewatering activities as well as site stormwater. The Harris County TRT also endorses EPA's Proposed Cleanup Plan to develop a comprehensive erosion and dust mitigation strategy prior to mobilization including temporary cover(s) within the exposed waste pit area(s) during the excavation process. We encourage the EPA to develop a sustainable execution plan that incorporates use of these temporary cover materials into the permanent cover and fill for the Site.

Although the Harris County TRT agrees with the dry excavation approach, we recommend that the EPA investigate the use of single mobilization/demobilization including installation of the sheet pile cofferdam around the entire excavation footprint. The work within the cofferdam could be performed in multiple stages to reduce risk of erosion of contaminated sediment in the event a flood occurred during remediation. However, we do not see a need to perform mobilization and sheet pile installation in multiple stages, which would increase costs.

The Harris County TRT agrees with the EPA that onsite passive/active dewatering of the excavated waste material would decrease subsequent costs of transportation and disposal by decreasing the mass of material as well as decrease risk(s) of spills during transportation to an off-site disposal facility. Unless mandated by the designated disposal facility, on-site stabilization by the addition of Portland Cement or another bulking agent would increase the mass of material to be transported and disposed of in an off-site landfill. The Harris County TRT recommends dewatered sediment that meets a designated dryness threshold (e.g. pass paint filter test and no free liquid in transport vehicles) be sealed in "burrito bags" and safely transported by truck and/or rail to an appropriate disposal facility.

VII. Request for Third-Party Oversight

Given the complexity of the remedial design, the risk of dioxin exposure to the environment, the Harris County TRT requests that the EPA increase the level of oversight to ensure that the objectives for overseeing PRP conducted RD/RAs are met. As set forth in EPA guidance over 25 years ago, EPA's two objectives for overseeing PRP conducted RD/RAs are to 1) ensure that the remedies are protective of public health and the environment throughout the life of the project; and 2) ensure the Remedial Action is implemented in compliance with the terms of the Settlement Agreement.[7] To ensure compliance and provide unbiased quality assurance monitoring of the Remedial Action, EPA Guidance introduced the concept of using an "Independent Quality Assurance Team."[8] Typical functions of the Independent Quality Assurance Team were to:

---

[7] OSWER, EPA. April 1990. Guidance on EPA Oversight of Remedial Designs and Remedial Actions Performed by Potentially Responsible Parties. Interim Final OSWER Directive 9355.541. p. 1-1.

[8] *Id*, p 2-2.

- Review design criteria, plans, and specifications for clarity and completeness;
- Direct and perform observations and tests for quality assurance inspection activities;
- Verify that the Construction Quality Control Plan is implemented in accordance with the site-specific Construction Quality Assurance Plan;
- Perform independent on-site inspections of the work to assess compliance with design criteria, plans and specifications; and
- Verify that equipment used in testing meets the test requirements and that the tests are conducted according to standardized procedures; and report to the PRP and EPA the results of all inspections and corrective actions, including work that is not of acceptable quality or that fails to meet the specified design requirements.[9]

The EPA Guidance also contemplated using an Oversight Official with a contractual agreement with the EPA to report directly to the Remedial Project Manager (RPM), providing technical support to the RPM. Although the Independent Quality Assurance Team is often retained by the PRP under the oversight of the Oversight Official, the necessity of having a completely unbiased and objective Quality Assurance team makes it preferable to use the Oversight Official to provide Independent Quality Assurance Team services in cases like the present.[10]

EPA Guidance has long recognized that the level of oversight is dependent on the complexity of the remedy and the past performance of the PRPs.[11] Reforms to EPA policy on Superfund PRP Oversight were predicated on the PRPs' ability and willingness to comply with settlement agreements and adhere to Agency standards.[12] In making reforms to PRP Oversight policy, the EPA recognized that where PRPs are not fulfilling their responsibilities under a settlement, the EPA has the responsibility to continue strict oversight procedures.[13] Only where PRPs' contractors have shown themselves to be reliable and technically competent is it recommended that procedures such as sporadic inspections, rather than continuous oversight, be implemented.[14]

Oversight reforms are intended to reward PRPs and their contractors who have conducted themselves appropriately and have developed trust with the EPA, the State, and the community. This is not the case at the Dioxin Pits. Accordingly, the EPA should contract with an Independent Quality Assurance Team to supervise the cleanup full time. The Independent Quality Assurance Team should regularly report to the EPA to ensure that the remedial design is strictly followed and BMPs are being implemented. The EPA should closely monitor all cleanup actions even splitting samples with the responsible parties, as appropriate. The Harris County TRT and Harris County citizens will have better peace of mind knowing that an Independent Quality Assurance Team is closely monitoring the remedial activities. In addition, the PRPs have demonstrated throughout the Superfund Process that their work on this Site in implementing the EPA's remedy requires independent oversight and monitoring.

---

[9] *Id*, p 2-6.
[10] *Id*, p. 5-5.
[11] *Id*, p. 5-1.
[12] May 17, 2000 Interim Guidance on Implementing the Superfund Administrative Reform on PRP Oversight, OSWER Directive No. 9200.0-32P, p. 2.
[13] *Id*, p. 2-3.
[14] *Id*, Attachment, par. 1.

Harris County Attorney filed an environmental enforcement action against the PRPs in State district court for civil penalties for the discharge of historic pollution from the Dioxin Pits. During the lawsuit, Harris County uncovered the following evidence:

- The PRPs produced emails of their intent to intimidate EPA officials.
- Additional emails discuss "build[ing] a global consensus" to make capping the preferred final remedy well before the RI/FS was completed so they could avoid "facing a dig and haul/burn as part of the final remedy."
- During depositions, consultants' project managers refused under oath to support their own reports.
- During depositions, consultants refused to identify who wrote specific portions of the reports.
- During depositions, consultants claimed not to know the qualifications of the various contributors to the reports.
- During depositions, the Dioxin Pit Project Manager refused to answer a direct question on whether she was an objective scientist or an advocate for the PRPs.

In addition to the matters uncovered during Harris County's litigation, the PRPs conduct during the Superfund process justifies the EPA requiring third-party oversight. Highlights of the conduct and other matters that have occurred during the Superfund process include:

- EPA took over the final drafting of the Revised Final Removal Action Completion Report and the RI/FS from PRPs and their consultants. If PRPs were unable to complete the Removal Action Completion Report and the RI/FS, then they should not be entrusted to implement the final remedy without independent oversight.
- As noted above, the Proposed Cleanup Plan identifies the numerous failures of the temporary armored cap. Since its installation, the PRPs have conducted periodic investigations and bathymetric surveys designed to monitor the integrity of the cap. However, it wasn't until the EPA Dive Team investigated the cap in late 2015 that numerous gaps in the cap were uncovered, including one approximately 500 square feet in size. The failure of the PRPs and their consultants to identify these significant structural failings is further evidence of the need for third-party oversight.
- The EPA disclosed in October 2016 that an 8 foot deep scour had been discovered adjacent to the eastern side of the temporary cap. The scour was officially reported in a memorandum to the EPA on September 20, 2016, but the scouring appears to have been documented by the PRPs and their consultants in July. This reporting delay is just another example of the PRPs management of the Dioxin Pits, which pose significant health and safety risks to the public.

For all of these reasons and the considerations that led to the EPA promulgating the Oversight Manual, the Harris County TRT requests that the EPA require the PRPs to undergo the third-party oversight discussed above as part of any final remedy for the Dioxin Pits.

VIII. Potential Impact on Harris County Parks

Harris County owns and operates three public parks in the vicinity of the Dioxin Pits. All three parks are located within the 100 year floodplain and are therefore at risk if there were any releases from the Dioxin Pits, particularly during a major storm event or hurricane. A map of the nearby County parks is attached as Exhibit B. Not only are the parks further justification for Harris County to applaud the EPA's decision for full removal, they are further justification for the Harris County TRT to request that the public be protected during the removal process. The Harris County TRT requests the EPA require the PRPs to consider off-site impacts should a release occur during cleanup, and especially include the nearby Harris County Parks as all Harris County citizens may make use of the parks and recreational fishing in its nearby waters. This review should include determining and providing appropriate warning to the public, placing limitations on public access and use, and monitoring for contamination and possible remediation if necessary.

IX. Local Federal and County Officials Support Removal

A large and bipartisan group of legislators representing residents affected by the Dioxin Pits has publicly stated their support for full removal, including U.S. Representatives Brian Babin (R-TX 36th District), Gene Green (D-TX 29th District), Randy Weber (R-TX 14th District), Sheila Jackson Lee (D-TX 18th District), Ted Poe (R-TX 2nd District), and Pete Olson (R-TX 22nd District); State Representatives Ed Thompson (R, District 29), Ana Hernandez (D, District 143), and Dennis Bonnen (R, District 25); and State Senator Sylvia Garcia (D, District 6). A number of these legislators have written letters to the EPA expressing their support for the full removal remedy. Additionally, several of them have spoken on the issue to local media.

"I just think it is a no-brainer that we will never be able to secure that site until it's taken out completely," Rep. Babin told a local news outlet. "The hundred-year cap that was put on this thing is now leaking like a sieve after just five years . . . We don't want to leave something like this as a legacy to our kids and our grandkids."[15]

Rep. Poe told a reporter, "I support the EPA's efforts for a full removal of the waste. Action is long overdue."[16] Rep. Lee also gave her support for full removal, saying, "I think there has to be a full and complete remediation. I want to emphasize that this about human life. This is about children."[17]

These legislators are joined by an array of Harris County departments and officials, united in their support for the full removal remedy. The Harris County Pollution Control Services Department, Harris County Public Health Department, Harris County Engineering Department, Harris County Flood Control District, and Harris County Attorney Vince Ryan have all written letters to the EPA supporting full removal. Many of these departments are an integral part of the Harris County TRT that sponsors these comments.

---

[15] Greg Groogan, *Congressmen call for Dioxin dump removal*, Fox 26 Houston, July 29, 2016, http://www fox26houston.com/news/183374834-story.

[16] Greg Groogan, *Increasing amount of Congress members calling for dump clean-up*, Fox 26 Houston, Aug. 12, 2016, http://www fox26houston com/news/189651496-story.

[17] Greg Groogan, *Congressional leaders call for removal of Dioxin dump*, Fox 26 Houston, Aug. 9, 2016, http://www.fox26houston.com/news/187452509-story

X. Documents Previously Submitted

The Harris County TRT requests the agency formally consider in its review all letters and documents and data previously submitted on behalf of and by Harris County. In addition to and including these documents and data previously submitted on behalf of and by Harris County, the Harris County TRT also urges the EPA to consider all documentation set forth in the table attached as Exhibit C.

CONCLUSION

The Harris County TRT appreciates the opportunity to provide our comments to the EPA regarding the Proposed Cleanup Plan. The Harris County TRT requests that the EPA select alternatives 6N and 4S, enhanced by our recommendations above as the final remedy. The Proposed Cleanup Plan along with the more conservative cleanup levels discussed above is the only alternative that ensures the long-term protection of Harris County residents and the environment. If you have any questions regarding our comments, we would welcome the opportunity to provide additional clarity.

Sincerely,

Bob Allen

Bob Allen
Director
Harris County Pollution Control Services Department
John Phelps Courthouse Annex 4
101 South Richey, Suite H
Pasadena, Texas 77506
Direct line: (713) 274-6416

Attachments

cc: *Via Email*
John Blount, HCED
Russ Poppe, HCFCD
Michael Schaeffer, HCPHD
Sam Coleman, EPA
David Gray, EPA
Carl Edlund, P.E., EPA
Anne Foster, EPA

References

Burkhard, L. 2009. Estimation of biota sediment accumulation factor (BSAF) from paired observations of chemical concentrations in biota and sediment. U.S. Environmental Protection Agency Ecological Risk Assessment Support Center. Cincinnati, OH. EPA/600/R-06/47.

Dean, K. E., Suarez, M. P., Rifai, H. S., Palachek, R. M., & Koenig, L. (2009). Bioaccumulation of Polychlorinated Dibenzodioxins and Dibenzofurans in Catfish and Crabs along an Estuarine Salinity and Contamination Gradient. *Environmental Toxicology and Chemistry, 28*(11), 2307-2317. Attached as Exhibit D.

Dutton, R.B., S.M. Holland, S. Choi, and G. Matlock. 1988. Characteristics, Attitudes, and Preferences of Shore-Based Spring Black Drum Anglers in Galveston May, Texas. Management Data Series Number 151.

OSWER, EPA. April 1990. Guidance on EPA Oversight of Remedial Designs and Remedial Actions Performed by Potentially Responsible Parties. Interim Final. OSWER Directive 9355.541.

PBS&J and Parsons. 2001. Dioxin Sediment and Tissue Sampling in Houston Ship Channel and Upper Galveston Bay: Final Report. Prepared for the Clean Rivers Program and Houston-Galveston Area Council.

Texas Parks and Wildlife Department, Austin, Texas. 28 pp. Accessed Oct 19, 2016 at http://tpwd.texas.gov/publications/pwdpubs/media/mds_coastal/Series%201_MDS151.pdf.

Texas Department of State Health Services. 2013. Characterization of Potential Adverse Health Effects Associated with Consuming Fish from the San Jacinto River-Houston Ship Channel; Harris County, Texas.

University of Houston and Parsons. 2013. Data analysis report: Survey of polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PCDFs) in the Galveston Bay system (GBS). 582-10-90494-19. Prepared in cooperation with the Texas Commission on Environmental Quality and U.S. Environmental Protection Agency. August 2013. Available through https://www.tceq.texas.gov/waterquality/tmdl/26-hscdioxin.html.

USEPA. 2000. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories. Volume 2: Risk Assessment and Fish Consumption Limits. Third Edition. EPA 823-B-00-008. Office of Water. Washington, DC. 383 pp.

USEPA. 2004. Economic and Benefits Analysis for the Final Section 316(b) Phase II Existing Facilities Rule. EPA-821-R-04-005. Office of Water. Washington, DC. 180 pp. Accessed Oct 19, 2016 at https://www.epa.gov/sites/production/files/2015-04/documents/cooling-water_phase-2_economics_2004.pdf.

U.S. Department of the Interior, U.S. Fish and Wildlife Service, and U.S. Department of Commerce. 2014. 2011 National Survey of Fishing, Hunting, and Wildlife-Associated Recreation. FHW/11-NAT (RV). Revised February 2014. 172 pp. Accessed Oct 19, 2016 at https://www.census.gov/prod/2012pubs/fhw11-nat.pdf.

Exhibits

Exhibit A	Dioxin Remediation Goals at Superfund Sites
Exhibit B	Map of Harris County Parks near Dioxin Pits
Exhibit C	Documents for Consideration
Exhibit D	Dean, K. E., *et al.*, Bioaccumulation of Polychlorinated Dibenzodioxins and Dibenzofurans in Catfish and Crabs along an Estuarine Salinity and Contamination Gradient. (2009)

Exhibit A

Exhibit A

Dioxin Remediation Goals at Superfund Sites

Project	ROD Date	Site	Medium	Site Location	Remediation Goal in ng/kg (part per trillion)		Comments
					2,3,7,8,-TCDD	Dioxin TEQ	
McCormick & Baxter	Mar-99	Stockton, CA	Soil (vadose zone)	Subareas X & Y		1000	dry weight, organic carbon normalized
			Sediment	Old Mormon Slough		21	
Commencement Bay/Nearshore Tideflats	Aug-03 [1]	Tacoma, WA	Surface Sediment	Olympic View Resource Area		20	SQC
			Surface Sediment			7.4	site-specific background goal
Coleman Evans Wood	Sep-06	Whitehouse, FL	Soil			30	clean up goals - on facility
Preserving Company						7	clean up goals - off facility
Pownal Tannery	Sep-09 [3]	Pownal, VT	Soil	Site-wide		1000	recreational use
Sonford Products - OU2	Sep-10	Flowood, MS	Soil	Onsite Op's Area		1000	industrial zoning
			Hydric Sediment	Wooded Area		450	
			Surface Soil	Offsite Residential		78	
			Surface Water	Onsite Stream		10	
	Sep-11	Anniston, AL	Groundwater			0.03	

Anniston PCB Site - OU3			Soil			-	value below calculated cancer risk range
Centerdale Manor Restoration	Sep-12	North Providence, RI	Sediment	Allendale Reach	15	34	
			Sediment	Lyman Mill Reach	15	24	
			Floodplain Soil	Allendale Floodplain	17		
			Floodplain Soil	Lyman Mill Floodplain	17	35	
			Soil	Source Area	17		
			Groundwater	Source Area			**i.e. 30 pg/L**
			Fish Tissue	A & LM Reaches	2.2	4.4	
Lower Duwamish Waterway [2]	Feb-13 [3]	Seattle, WA	Surface Sediment	site-wide		2	top 10 cm
			Surface Sediment	site-wide		37	top 45 cm
			Surface Sediment	clamming areas		13	top 45 cm
			Surface Sediment	individual beaches		28	top 45 cm
			Fish Tissue	site-wide		0.35	may be adapted in the ROD
			Crab - meat			0.53	
			Crab - whole body			2	
			Clams			0.71	
Portland Harbor [2]		Portland, OR	Surface Sediment	site wide	0.6 to 2		Sites B, C, D = 0.0006 µg/kg
							Sites E, F, G = 0.002 µg/kg
Diamond Alkali	Mar-16	Essex & Hudson Counties NJ	Sediment	Lower 8 Miles of the Lower Passaic River	8.3		based on 56 fish meals per year

Exhibit B

HARRIS COUNTY OWNED PARKS
Potentially Affected by San Jacinto River Waste Pits Superfund Site

(south of I-10)

Exhibit C

Exhibit C
Documents in Administrative Record for Consideration

DOCID	DATE	TITLE	AUTHOR	SUMMARY	ANCHOR & INTEGRAL MENTIONS
9186095	5/6/2010	LETTER REGARDING SAN JACINTO RIVER WASTE PITS SUPERFUND SITE COMMENTS ON DRAFT REMEDIAL INVESTIGATION FEASIBILITY STUDY WORK PLAN	Palacio, Herminia (HARRIS COUNTY PUBLIC HEALTH AND ENVIRONMENTAL SERVICES)	Comments on Draft RI/FS including suggested revisions to site background sections and request to include pit areas not covered by the draft	
9182298	5/19/2010	[HARRIS COUNTY PUBLIC HEALTH AND ENVIRONMENTAL SERVICES COMMENTS ON DRAFT REMEDIAL INVESTIGATION/FEASIBILITY STUDY WORK PLAN	Palacio, Herminia (HARRIS COUNTY PUBLIC HEALTH & ENVIRONMENTAL SERVICES)	See above.	
611000	6/11/2010	COMMENTS ON DRAFT TIME CRITICAL REMOVAL ACTION ALTERNATIVE ANALYSIS	Palacio, Herminia (HARRIS COUNTY PUBLIC HEALTH & ENVIRONMENTAL SERVICES)	Response to Draft Time Critical Removal Action Analysis, including request to design TCRA to withstand a 100-year flood, transport of dioxin on colloid particles, and critique of analyses of alternatives	Response to 2010 TCRA
9344979	7/6/2010	COMMENTS ON DRAFT TIME CRITICAL REMOVAL ACTION ALTERNATIVES ANALYSIS FROM HARRIS COUNTY PUBLIC HEALTH & ENVIRONMENTAL SERVICES - SAN JACINTO	Palacio, Herminia (HARRIS COUNTY PUBLIC HEALTH AND ENVIRONMENTAL SERVICES)	Reiterates comments about 100-year floods and dioxin on colloids, and advocating a mix of Alternatives 3,4, and 5	
636911	12/21/2010	MEMORANDUM OF UNDERSTANDING BETWEEN HARRIS COUNTY AND EPA	Patel, Snehal, R (HARRIS COUNTY)	Establishing partnership between EPA Region 6 and Harris County outlining roles of EPA, TCEQ, trustees, and County	
637762	6/23/2011	HARRIS COUNTY COMMENTS REGARDING DRAFT ADDENDUM 2 TO THE SOIL SAMPLING AND ANALYSIS PLAN FOR RESIDENTIAL SOIL SAMPLING - SAN JACINTO RIVER WASTE PIT	None (HARRIS COUNTY)	Comments on SAP for soil sampling, including clarifying unclear statements and requesting the total number of samples collected	
637761	6/30/2011	TEXAS DEPARTMENT OF STATE HEALTH SERVICES COMMENTS REGARDING SAN JACINTO RIVER WASTE PITS HEALTH ASSESSMENT-PUBLIC COMMENT DRAFT	Allen, Bob (HARRIS COUNTY POLLUTION CONTROL SERVICES DEPARTMENT)	Comments to Health Assessment, including that it did not collect independent samples, and recommending additional sampling and a follow up of residents in surrounding neighborhoods.	
9340603	3/2/2012	DRAFT REMEDIAL ALTERNATIVES MEMORANDUM - PCS COMMENTS	Vancas, Cecilia (HARRIS COUNTY OF)	Comments re. assumptions in the memo, Critical Site Restrictions section, and the memo's treatment of erosion	
9340602	3/2/2012	DRAFT TOXICOLOGICAL AND EPIDEMIOLOGICAL STUDIES MEMORANDUM (TEMS) PCS COMMENTS 03/02/2012	Babin, Latrice (HARRIS COUNTY OF)	Requesting area to include Baytown and Channelview in addition to Highlands, to study acute exposure effects, and use of dermal "absorbed dose" toxicological criteria,	
9340371	3/9/2012	POLLUTION CONTROL SERVICES COMMENTS ON THE 03/09/2012 DRAFT EXPOSURE ASSESSMENT	Allen, Bob (HARRIS COUNTY OF)	Email from Latrice Babin outlining comments on chemistry data for evaluating exposures.	

		MEMORANDUM FOR SAN JACINTO RIVER WASTE PITS			
670157	6/25/2012	HARRIS COUNTY POLLUTION CONTROL SERVICES COMMENTS ON FINAL WORK PLAN - SAN JACINTO RIVER WASTE PITS	Allen, Bob (HARRIS COUNTY POLLUTION CONTROL SERVICES DEPARTMENT)	Email from Chris Barry regarding the need for a definition of MQL that is distinct from that for MRL.	
9549108	7/25/2012	PROVISION OF EROSION PHOTOS FOR POWERPOINT FOR 07/25/2012 CAC MEETING	Babin, Latrice (HARRIS COUNTY OF)	Photos.	
100001100	1/15/2013	[REDACTED] [SUBMITTAL OF DOCUMENTATION THAT SEAFOOD IS BEING HARVESTED FROM THE SAN JACINTO RIVER	Ryan, Vince (HARRIS COUNTY)	Affidavits of Texas Parks & Wildlife Game Warden and fishermen regarding seafood harvesting and consumption. Draft Public Outreach Action Items for residents	
9477677	10/17/2013	HARRIS COUNTY COMMENTS ON DRAFT FEASIBILITY STUDY, WITH ATTACHMENTS	None (HARRIS COUNTY CLERKS OFFICE)	Comments include that recommendation to remove waste wasn't included and should have been and more specific critiques of analysis of alternatives; attachments include studies referenced in comments.	Extensive comments on Anchor Draft FS
9495093	12/17/2013	FINAL COMMENTS REGARDING FEASIBILITY STUDY - SAN JACINTO	None (HARRIS COUNTY CLERKS OFFICE)	See above	Extensive final comments on Anchor's FS
9494969	1/30/2014	MEMORANDUM REGARDING COMMUNITY MEETING WITH EPA - SAN JACINTO	Wehr, Michael (HARRIS COUNTY POLLUTION CONTROL SERVICES)	Memo from Michael Wehr summarizing a community meeting to discuss the Draft FS, including the meeting agenda and materials distributed.	
100001070	3/6/2014	[REDACTED] [COMMENTS REGARDING POTENTIAL LOCATIONS FOR SEAFOOD ADVISORY SIGNS - SAN JACINTO]	Owens, Rock, W (HARRIS COUNTY)	Emails with comments from Scott Jones, Michael Tennant, and Rock Owens re: sign locations.	
9521169	5/1/2014	HARRIS COUNTY RECOMMENDATION FOR REMEDY OF SAN JACINTO RIVER WASTE PITS	Ryan, Vince (HARRIS COUNTY OF), R06. Soard, Robert, W (HARRIS COUNTY), R06: O-Rourke, Terence (HARRIS COUNTY)	Letter to NRRB outlining Harris County's recommendations, including extensive site background and and arguments for full removal.	Detailed history and arguments for county proposal, responses to Anchor recommendations
9668908	5/6/2014	HARRIS COUNTY PRESS RELEASE- COUNTY ATTORNEY VINCE RYAN URGES EPA TO REQUIRE COMPLETE DIOXIN REMOVAL FROM SAN JACINTO RIVER WASTE PITS	Ryan, Vince (HARRIS COUNTY)	Press release summarizing above letter.	
9563812	7/15/2014	HARRIS COUNTY REQUESTS IMPLEMENTATION OF AN INVESTIGATION TO ENSURE THE PROTECTION OF PUBLIC SAFETY AND THE ENVIRONMENT IN CONNECTION WITH THE SAN JACINTO RIVER WASTE PITS SITE	Owens, Rock (HARRIS COUNTY OF)	Letter to Anne Foster, EPA requesting a formal investigation by third party because documents used for RI/FS were prepared for litigation Attachments: Affidavits of Francis Chin and Elton Parker; Depo transcripts of David Keith and Jennifer Sampson White; Samuel Brody Flood Risk Assessment	Extensive arguments on reliability of Anchor documents

9645485	7/21/2014	HARRIS COUNTY ADDITIONAL COMMENTS AND INFORMATION REGARDING ALTERNATIVE METHODS TO REMEDIATE THE SAN JACINTO RIVER WASTE PITS SITE	Owens, Rock (HARRIS COUNTY OF), R06· Ryan, Vince (HARRIS COUNTY OF)	Comments including that construction methods can affect resuspension rates; effective methods include sheet pile walls, limiting dredging to small areas at a time, berms, and weather monitoring.	Additional comments to FS alternatives
9563268	8/15/2014	HARRIS COUNTY TECHNICAL REVIEW TEAM COMMENTS ON INDEPENDENT REVIEW SCOPE OF WORK - SAN JACINTO RIVER WASTE PITS SITE	None (HARRIS COUNTY CLERKS OFFICE)	Recommendations for scope of work of independent review, including analysis of river hydraulics & sediment transport, assessment of groundwater and pore water concentrations, analysis of remedial alternatives, risk assessment, integrity of RI/FS, identify & review data withheld	Identifies areas of Anchor documents in need of review
9559390	2/24/2015	HARRIS COUNTY CONCERNS AND REQUESTS REGARDING SIGNIFICANT GROUNDWATER AND SURFACE WATER ISSUES AT THE SAN JACINTO RIVER WASTE PITS - TRACKING NO. 7011 1570 0000 7520 1957	Ryan, Vince (HARRIS COUNTY OF), R06. Owens, Rock, W (HARRIS COUNTY)	Letter to EPA re· insufficient groundwater data, problems with a capping approach, and bias in the RI/FS process,	Addresses concerns about Anchor data and integrity of RI/FS process
9645481	2/24/2015	HARRIS COUNTY REQUEST THAT EPA REQUIRE A COMPLETE REVIEW OF THE GROUNDWATER MONITORING PLAN, TESTING METHODS, DATA AND TEST RESULTS FOR SAN JACINTO RIVER WASTE PITS - TRACKING NO. 7011 1570 0000 7520 1957	Owens, Rock (HARRIS COUNTY OF), R06. Ryan, Vince (HARRIS COUNTY OF)	No new content - Includes letter above and 7/15/14 letter.	
9633800	5/27/2015	NOTICE OF POSSIBLE FLOODING REGARDING INSPECTION OF SAN JACINTO RIVER WASTE PITS SITE CAP	Allen, Bob (HARRIS COUNTY POLLUTION CONTROL SERVICES DEPARTMENT)	Email from Bob Allen alerting Gary Miller of flooding on date of planned inspection	
9645504	6/19/2015	HARRIS COUNTY TECHNICAL REVIEW TEAM ADDITIONAL SAMPLING PLAN RECOMMENDATIONS - SAN JACINTO RIVER WASTE PITS	None (HARRIS COUNTY CLERKS OFFICE)	Sampling recommendations· Northern impoundment area (groundwater, surface water, sediment & pore water), southern impoundment area (groundwater, sediment & pore water). Includes maps of area with reference sites	
9673780	7/2/2015	HARRIS COUNTY REQUEST FOR MEETING TO DISCUSS ON-GOING EFFORTS TO ADDRESS THE ADVERSE HUMAN HEALTH AND ENVIRONMENTAL EFFECTS - SAN JACINTO RIVER WASTE PITS	Ryan, Vince (HARRIS COUNTY)	Letter requesting meeting with EPA for input on use of civil penalties and to discuss EPA's authority to order IP to produce documents for public consideration	
9595057	7/15/2015	HARRIS COUNTY CORRESPONDENCE REGARDING REQUEST TO RETAIN AN INDEPENDENT THIRD PARTY TO CONDUCT A FORMAL INVESTIGATION FOR SAN JACINTO RIVER WASTE PITS	Owens, Rock (HARRIS COUNTY OF)	Repeat entry, see 9563812	
9595056	8/15/2015	HARRIS COUNTY COMMENTS REGARDING INDEPENDENT REVIEW SCOPE OF WORK REQUEST BY EPA FOR SAN JACINTO RIVER WASTE PITS	None (HARRIS COUNTY CLERKS OFFICE)	Repeat entry, see 9563268	

9674053	9/10/2015	HARRIS COUNTY TECHNICAL REVIEW TEAM COMMENTS ON U.S. ARMY CORPS ENGINEER FEASIBILITY STUDY EVALUATION OF SAN JACINTO WASTE PITS	Allen, Bob (HARRIS COUNTY POLLUTION CONTROL SERVICES DEPARTMENT)	Advocating full remedial alternative, addressing problems in USACE Report and with other alternative remedies	Addresses problems with sections USACE imported from Anchor models
9643960	11/24/2015	HARRIS COUNTY TECHNICAL REVIEW TEAM COMMENTS ON DRAFT SEDIMENT AND POREWATER SAMPLING PLANS FOR THE SAN JACINTO RIVER WASTE PITS	: None (HARRIS COUNTY POLLUTION CONTROL SERVICES DEPARTMENT)	Reviewing two Anchor & Integral SAP documents, comments/critiques on methodology	Comments to A&I Sampling & Analysis Plans
975956	8/15/2016	HARRIS COUNTY ENGINEERING DEPARTMENT RECOMMENDATION TO REMOVE THE WASTE	Blount, John (HARRIS COUNTY)	Letter advocating full removal.	
100000960	9/1/2016	HARRIS COUNTY PUBLIC HEALTH BELIEVES THAT THE DIOXIN WASTE AT THE SAN JACINTO RIVER WASTE PITS SHOULD BE ENTIRELY REMOVED FROM THE SITE	Shah, Umair, A (HARRIS COUNTY PUBLIC HEALTH AND ENVIRONMENTAL SERVICES)	Letter advocating full removal.	
9563561	6/10/2014	CONGRESSMAN GREEN COMMENTS AND RECOMMENDATION TO SELECT ALTERNATIVE 6N FROM DRAFT FEASIBILITY STUDY TO REMOVE DIOXIN WASTE]	Green, Gene (U.S. HOUSE OF REPRESENTATIVES)		
9689100	2/17/2016	[CONGRESSIONAL INQUIRY FROM REPRESENTATIVE GENE GREEN REGARDING SAN JACINTO RIVER WASTE PITS SUPERFUND SITE	[CONGRESSIONAL INQUIRY FROM REPRESENTATIVE GENE GREEN REGARDING SAN JACINTO RIVER WASTE PITS SUPERFUND SITE		
975958	8/9/2016	TEXAS STATE REPRESENTATIVE RECOMMENDATION OF FULL REMOVAL	Thompson, Ed (TEXAS HOUSE OF REPRESENTATIVES)		
500023012	8/1/2016	STATE HOUSE REPRESENTATIVE DISTRICT 143, ANA HERNANDEZ, REQUEST FOR FULL REMOVAL OF THE SAN JACINTO RIVER WASTE PITS	Hernandez, Ana (TEXAS HOUSE OF REPRESENTATIVES)		
500022881	7/13/2016	[TEXAS STATE HOUSE REPRESENTATIVE DISTRICT 25, DENNIS BONNEN, URGING FOR REMOVAL OF THE SAN JACINTO RIVER WASTE PITS	: Bonnen, Dennis (TEXAS HOUSE OF REPRESENTATIVES)		
500022879	7/13/2016	TEXAS STATE SENATOR DISTRICT 6, SYLVIA R GARCIA, URGING REMOVAL OF THE SAN JACINTO RIVER WASTE PITS]	Garcia, Sylvia (TEXAS STATE SENATE)		

Exhibit D

Environmental Toxicology and Chemistry, Vol 28, No 11, pp 2307-2317, 2009

© 2009 SETAC

Printed in the USA
0730-7268/09 $12 00 + 00

BIOACCUMULATION OF POLYCHLORINATED DIBENZODIOXINS AND DIBENZOFURANS IN CATFISH AND CRABS ALONG AN ESTUARINE SALINITY AND CONTAMINATION GRADIENT

KIRK E. DEAN,*† MONICA P. SUAREZ,† HANADI S RIFAI,‡ RANDY M. PALACHEK,† and LARRY KOENIG§
†Parsons Corporation, 8000 Centre Park Drive, Suite 200, Austin, Texas 78754-5140, USA
‡Department of Civil and Environmental Engineering, University of Houston, 4800 Calhoun, Houston, Texas 77204-4003, USA
§Texas Commission on Environmental Quality, MC-203, P O Box 13087, Austin, Texas 78711-3087, USA

(*Received* 17 *December* 2008, *Accepted* 15 *June* 2009)

Abstract—Elevated but variable levels of polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/Fs) were observed in hardhead sea catfish (HH) and blue crabs (BCs), as well as in water and sediment, of the Houston Ship Channel system, Texas, USA It is hypothesized that the variation was caused by the spatial variability of PCDD/F contamination, together with the natural mobility of organisms in satisfying prey, temperature, salinity, and reproductive requirements Structural equation modeling was applied to explore the congener-specific relationships between PCDD/F levels in HH and BC tissues and independent predictors such as PCDD/F contamination levels, environmental factors such as salinity and temperature, temporal–spatial factors such as site depth and season, and biological factors such as length, weight, and lipid content Contamination levels in both sediment and water were statistically significant predictors of the levels of less chlorinated congeners in both HH and BCs, with the standardized regression weight for sediment concentration roughly twice that for the water concentration This implies that sediments are the dominant route for PCDD/F exposure and remediation efforts should focus on legacy sediment contamination Tissue lipid content was a significant predictor of tissue concentrations in HH but only to a lesser extent in BCs, perhaps due to their low lipid content Site depth and seasonal factors also were significant predictors of tissue concentrations For the highly chlorinated congeners, only a small fraction of the variance in tissue concentrations was explained by the independent predictors, possibly indicating that uptake and elimination kinetics, biotransformation processes, or both may be more important factors controlling the bioaccumulation of those congeners

Keywords—Dioxin   Bioaccumulation   Structural equation modeling

INTRODUCTION

Elevated levels of 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in hardhead sea catfish (*Ariopsis felis* Linnaeus, HH) and blue crabs (*Callinectes sapidus* Rathbun; BCs) of the Houston Ship Channel (HSC; Houston, TX, USA) system were first observed by the Texas Department of Health in 1990. Seafood consumption advisories were issued for these species at that time. Elevated PCDD/F levels have also been observed in water and sediments of the system [1] Although the sources of contamination are believed to be primarily historical, contaminated sediments continue to serve as an internal source of PCDD/Fs to the water bodies, supplemented by other continuing sources including atmospheric deposition, runoff, and industrial and domestic wastewaters [1,2]. The levels of PCDD/Fs in fish, particularly catfish, and BCs have not been observed to decline since they were first quantified in 1990 [1]. A better understanding of the bioaccumulation behavior of PCDD/Fs in fish and crabs in the HSC may provide more accurate estimates of loading reductions necessary to achieve safe thresholds for seafood consumption

Theory

Bioaccumulation involves the uptake of chemicals by aquatic organisms from their environment via multimedia exposures It can include direct uptake from the aqueous dissolved phase, via respiratory exchange or dermal transfer, and dietary exposure with gastrointestinal uptake In the equilibrium partitioning (EqP) model [3], the bioaccumulation of PCDD/Fs and other nonpolar hydrophobic organic compounds by aquatic organisms is commonly considered to be linearly related to the lipid content of the tissue (which indicates the sorptive capacity of the tissue), the fugacity of the contaminant in the system in which the organism is exposed, and the hydrophobicity of the contaminant (usually indicated by an octanol–water partition coefficient). The fugacity, or partial pressure, of the contaminant is the concentration in an environmental medium divided by the fugacity capacity of that medium [4] At thermodynamic equilibrium, the fugacities in various phases are equal. The soot or organic carbon content is commonly considered to control the fugacity capacity of sediments [5,6], while lipid content is considered to control the fugacity capacity of most tissues [7] In water, suspended solids and dissolved and colloidal organic carbon content may increase the fugacity capacity [8] Given efficient dietary uptake and minimal biotransformation, biomagnification of contaminants in the tissues of organisms can occur when tissue fugacities exceed those in the surrounding environment (water and sediments).

The bioaccumulation factor (BAF) has been defined by the U S Environmental Protection Agency (U S EPA) as the ratio (in liters per kilogram of tissue) of the concentration of a chemical in the tissue of an aquatic organism to its concentration in water in situations where both the organism and its food are exposed and the ratio does not change substantially over time [9]. Recognizing the importance of

* To whom correspondence may be addressed
(kirk dean@parsons com)
Published on the Web 7/16/2009

tissue lipid content on the fugacity capacity of tissue, and that of suspended solids and dissolved and colloidal organic content on the apparent fugacity capacity of water, the U.S. EPA also defined a baseline BAF as a BAF that is based on the concentration of chemical freely dissolved in water and the concentration of the chemical in the lipid fraction of tissue. The BAF is an equilibrium concept and accounts for uptake and elimination from all sources and processes, including uptake via the diet and across the gill surface. Similarly, a biota–sediment accumulation factor (BSAF) has been defined as the ratio (in kilograms of sediment organic carbon per kilogram of lipid) of the lipid-normalized concentration of a chemical in tissue of an aquatic organism to its organic carbon-normalized concentration in surface sediment in situations where the ratio does not change substantially over time, both the organism and its food are exposed, and the surface sediment is representative of average surface sediment in the vicinity of the organism.

Although the EqP model is useful in predicting the potential bioaccumulation of contaminants, many studies [10–17] have shown that it sometimes fails to accurately predict observed BAFs and BSAFs. Of particular concern with PCDD/Fs, large and extremely hydrophobic compounds may not achieve the levels of bioaccumulation predicted by the EqP model. Various explanations have been offered for these observations. Chemical fugacities in sediments may not be in equilibrium with those in the overlying water column, resulting in variable bioaccumulation depending on the major route of exposure of an organism (sediment versus water) and that of its prey [10] In addition, the EqP model does not account for variations in the composition of tissue lipids [18] and sediment organic matter [11,19] that affect bioavailability or fugacity capacity of these phases. The permeation of large molecules through cell membranes may be substantially hindered due to steric factors [11–13,20], thus limiting their bioaccumulation. Low dietary uptake efficiencies [14,15] and rapid elimination via feces [15,21] and biotransformation [10,15,16] may also limit the bioaccumulation for these compounds. Finally, the EqP model does not explicitly account for changes in an organisms' diet [11], reproductive status, nutritional status, growth [21,22], or mobility [17], to the extent that they occur at a rate faster than the compounds are taken up or eliminated from tissue.

The relative impact of water and sediments in determining bioaccumulation is of major interest to evaluating the effectiveness of various contamination remediation strategies. If the majority of contaminant bioaccumulation occurs via a sediment route, the remediation of legacy sediment contamination may be necessary On the other hand, if contaminant bioaccumulation occurs via a waterborne route, it may be more effective to achieve further reductions of ongoing discharges and deposition of PCDD/Fs to water

Study area

The HSC is a dredged channel 13.7 m deep and 162 m wide extending approximately 86 km from the Gulf of Mexico at Galveston to near downtown Houston. The lower 46 km of the HSC extend unconfined from the Gulf of Mexico through Galveston Bay, a large (1,317 km^2), shallow (2.1 m average depth) embayment The middle 15 km of the HSC from Morgan's Point up to the confluence with the San Jacinto River are partially confined, but numerous small, shallow embayments abut and connect to the HSC. Upstream of the confluence with the San Jacinto River, the HSC runs 25 km westward along Buffalo Bayou in a confined channel with several tributary bayous

The HSC–Galveston Bay system is tidally influenced, and freshwater inflow exerts a strong influence on salinity levels In most parts of Galveston Bay, salinities average 15‰, indicating approximately equal contributions of freshwater and saltwater. The salinities decline with distance upstream, and average salinities are approximately 6‰ in the upper reaches of the HSC In tidal tributaries to the upper reach of the HSC, salinities are often less than 1‰. Freshets occur throughout the year, associated with major rainfall events, but inflow is typically highest in April and May and lowest from July through October. A moderate vertical salinity gradient typically occurs in the deep channels, with denser saltwater inflows along the bottom and freshwater inflows on top However, vertical mixing tends to be strong in the system and the shallow bays are seldom stratified

Contamination due to PCDD/Fs is not uniform throughout the HSC system. Two areas in the upper reaches of the HSC system are particularly contaminated with PCDD/Fs [1,2] An industrial waste pit was operated in the 1960s and 1970s along the banks of the San Jacinto River near Interstate Highway 10. With land subsidence of several feet in recent decades, the waste pit was submerged in the San Jacinto River, likely causing substantial PCDD/F contamination throughout the HSC system. The level of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) exceeded 20,000 ng/kg dry weight in one sediment sample from this site. A more diffuse area of elevated PCDD/F levels in sediment occurs in the Buffalo Bayou portion of the HSC upstream of the confluence with the San Jacinto River, with TCDD levels as high as 650 ng/kg in sediments Levels of PCDD/Fs tend to decline with distance upstream and downstream from these two most contaminated areas, and PCDD/F levels in the water and sediment of upper Galveston Bay are much lower than in the more contaminated areas, with TCDD levels seldom exceeding 1 ng/kg in sediment. Concentrations of PCDD/Fs in water exhibit less spatial variation than those in sediment Median levels of TCDD in water were 1.1 pg/L near the most contaminated site in the San Jacinto River at Interstate Highway 10, 0 23 pg/L in the more contaminated areas of the HSC upstream of the San Jacinto River, and 0.05 pg/L in upper Galveston Bay.

Both BCs and HH live and feed primarily along the sediment surface and are opportunistic omnivores and scavengers that occupy a similar midtrophic level niche. The diet of HH in the HSC system is dominated by shrimp, crabs, stomatopods, organic detritus, and small fish [23] The diet of BCs includes mollusks, shrimp, crabs, small fish, plants, and organic detritus [24].

Both BCs and HH are sensitive to the temperature and salinity variations in a subtropical estuary. During winter months, when average water temperatures fall below 15°C, HH are rare in the HSC system and are believed to migrate into the deeper offshore waters of the Gulf of Mexico [25] Large volumes of freshwater inflow may also cause HH to migrate periodically from the upper and middle reaches of the HSC to the lower reaches of Galveston Bay and the Gulf of Mexico. McElyea [26] reported a strong positive correlation between HH abundance and salinity in the upper HSC.

Adult male BCs tend to prefer the low-salinity waters of the upper estuary and are the dominant sex in most of the HSC system, while females prefer salinities above 20‰ and migrate to the Gulf of Mexico to spawn [24] The abundance of BC in the upper HSC was observed to be positively correlated with temperature [26], and crabs may migrate to the deeper waters of the Gulf of Mexico or burrow into mud and enter a state of torpor during the winter [27]

The spatial variability of PCDD/F contamination in the HSC system, together with the mobility of HH and BCs (due to food availability, life cycles, and their environmental preferences for temperature and salinity conditions), results in spatially and temporally variable exposures to PCDD/Fs For risk assessment purposes, the seasonal and spatial variation in bioaccumulation was of particular interest Temporally and spatially uniform tissue fugacities (lipid-normalized concentrations) of PCDD/Fs would imply that the processes of biouptake and elimination were slow relative to the variations in PCDD/F exposures On the other hand, relatively constant BAFs and BSAFs would indicate that these species achieved rapid equilibrium with the exposure conditions at the site and time they were sampled

MATERIALS AND METHODS

At each site, approximately 700 L of water were pumped at a rate of 1.6 L/min through an Infiltrex 300 high-volume water sampling system (Axys Technologies). Water was first passed through a wound glass fiber filter cartridge (10 cm long × 6.4 cm diameter) with a 1-µm effective pore size in order to trap particle-associated PCDD/Fs The filtrate was then passed through a stainless steel column packed with approximately 250 g of Amberlite® XAD-2 hydrophobic cross-linked polystyrene resin (Rohm and Haas) to trap dissolved PCDD/Fs Experiments with two XAD-2 resin columns in series showed that they trapped dissolved PCDD/F efficiently, with little or no breakthrough to the second column. The PCDD/Fs associated with colloids such as humic substances were considered to pass through the XAD-2 columns at the neutral–high ambient pH of the HSC. Other investigators using similar hydrophobic resin columns observed that more than 90% of the dissolved and colloidal organic carbon passed through the columns [12,28]. However, the size of the colloidal pool of PCDD/Fs was not measured, nor was its passage through the XAD-2 cartridge verified Simultaneously with PCDD/F sampling, grab samples were collected for measurement of total suspended solids and total and dissolved organic carbon. Temperature, salinity, specific conductance, pH, and dissolved oxygen were measured with a YSI 600XLM sonde.

Surface (0–5 cm) sediment samples were collected with a stainless steel Ponar dredge. At each site, a minimum of three grab samples were deposited in a stainless steel bowl and mixed thoroughly with a stainless steel spoon. Composite subsamples were then deposited into a labeled, precleaned amber glass jar with a Teflon®-lined lid and stored at less than 4°C until analysis.

Biota samples

We collected HH and BCs from 45 sites throughout the HSC system during the spring, summer, and fall seasons from 2002 to 2004. Site locations are shown in Suarez et al. [2] A total of 108 paired HH, sediment, and water samples and 155 paired BC, sediment, and water samples were collected from the 45 sites

Hardhead catfish were collected using gill nets, fish traps, or hook and line All specimens were adults exceeding 28 cm in length. Blue crabs were collected using baited crab traps, and with few exceptions, all specimens exceeded the legal minimum carapace width of 12.7 cm. Specimens were weighed and measured, and then HH were filleted to extract muscle portions, and edible meat portions of BC were extracted. The selected tissues from each specimen were then composited and homogenized with two to four other specimens of the same species collected from the same site on the same date These were stored frozen until analysis.

An effort was made to collect the BC, HH, sediment, and water samples from a given site on the same day However, this proved difficult in practice and the samples from various media for a given station were collected as much as two weeks apart.

Chemical analyses

The levels of the 17 2,3,7,8-substituted tetra- through octa-chlorinated PCDDs and PCDFs in water, sediment, and tissue samples were quantified by high-resolution gas chromatography or high-resolution mass spectrometry using U.S EPA method 1613 revision B (www.epa.gov/waterscience/methods/method/dioxins/1613 pdf) at a U S EPA–certified commercial laboratory. Tissue lipid content was determined gravimetrically by U S. EPA method 1613B. Sediment organic carbon content was determined in a carbon, hydrogen, and nitrogen elemental analyzer following acidification for removal of inorganic carbon. Further details on analytical methods and quality control are provided in Suarez et al. [1,2].

Statistical analyses

Bioaccumulation factors and BSAFs were calculated for HH and BCs for each of the 17 congeners quantified for paired samples where PCDD/F concentrations were quantifiable in both the tissue and the sediment (for BSAFs) or in the water-dissolved phase (for BAFs) Both BAFs and BSAFs were calculated using lipid-normalized tissue concentrations.

Structural equation modeling (SEM), a multivariate statistical technique similar to multiple regression that describes a network of complex linear relationships among variables [29], was applied to ascertain the factors influencing bioaccumulation. Several potential influential factors related to PCDD/F concentrations in tissue (on a wet weight basis) were considered in exploratory SEM· PCDD/F concentrations in sediment and water (total, dissolved, and suspended), characteristics of the organisms (length, weight, length to weight ratio, and lipid content), water characteristics (temperature, salinity, pH, dissolved organic carbon, and suspended solids concentration), sediment organic carbon content, spatial variables (site depth and distance from various points), and temporal variables (year, season, month, Julian day number [1–365], and air temperature). The sampling site depth primarily distinguishes bay sites from the much deeper channel sites Factor analysis was used to extract from the spatial variables two major factors, one indicating the distance along the channel from downtown Houston toward the Gulf of Mexico and a second indicating the distance along the San Jacinto River channel. However, it was noted that the spatial factors strongly covaried with contaminant concentrations, thus, they were not used in further analyses. The air temperature used was the average air temperature in Houston from 1970 to 2000 for each Julian day number, which peaks in the summer and then declines, whereas the Julian day number increases throughout the year.

As preliminary results indicated that models attempting to apply to all congeners and both HH and BCs neither fit well nor explained much of the observed variation, separate SEMs were developed for each species, and for each congener with more

Table 1 Summary of measured 2,3,7,8-substituted polychlorinated dibenzodioxins and polychlorinated dibenzofurans congener concentrations in various media[a,b]

	Blue crab muscle, pg/g (n = 155)			Hardhead catfish fillets, pg/g (n = 108)			Dissolved concentration, pg/L (n = 148)			Sediment concentration, pg/g (n = 174)		
Congener	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max
2378-TCDD	<0 18	2 2	12	<0 36	5 15	26	<0 003	0 038	0 441	<0 23	6 45	650
12378-PeCDD	<0 10	<0 29	1 5	<0 10	0 36	4 5	<0 003	<0 007	0 028	<0 33	<0 85	13
123478-HxCDD	<0 09	<0 21	1 4	<0 10	<0 24	6 8	<0 003	0 009	0 035	<0 12	1 85	12
123678-HxCDD	<0 11	0 27	3 1	<0 11	0 64	7 6	<0 004	0 014	0 199	<0 29	3 95	71
123789-HxCDD	<0 10	<0 23	1 7	<0 11	0 29	7 5	<0 004	0 018	0 082	<0 48	3 60	24
1234678-HpCDD	<0 23	0 74	4 2	<0 41	1 15	10	0 030	0 416	4 27	1 90	120	2,100
12346789-OCDD	0 35	3 4	62	0 59	2 8	20	0 227	8 27	80 7	39	3,100	41,000
2378-TCDF	<0 21	3 8	30	<0 12	0 44	4 6	0 009	0 131	1 22	<0 16	18 5	1,600
12378-PeCDF	<0 10	<0 28	1 7	<0 07	<0 24	5 0	<0 003	0 010	0 199	<0 2	1 05	170
23478-PeCDF	<0 09	0 35	1 7	<0 12	0 54	4 4	<0 004	0 012	0 118	<0 23	1 80	180
123478-HxCDF	<0 09	<0 23	2 0	<0.07	<0 19	6 5	<0 002	0 012	0 242	<0 17	2 10	370
123678-HxCDF	<0 08	<0 20	1 6	<0 07	<0 22	7 8	<0 002	<0 009	0 257	<0 23	1 40	110
234678-HxCDF	<0 07	<0 21	1 6	<0 03	<0 21	7 5	<0 003	0 007	0 114	<0 19	1.30	51
123789-HxCDF	<0 07	<0 21	1 9	<0 03	<0 26	6 4	<0 001	<0 005	0 048	<0 20	0 67	88
1234678-HpCDF	<0 12	<0 39	14	<0 05	<0 36	9 0	<0 003	<0 054	2 21	<0 19	16 0	1,500
1234789-HpCDF	<0 10	<0 27	1 5	<0 04	<0 29	10	<0 002	<0 009	0 138	<0 25	1 70	160
12346789-OCDF	<0 21	1 0	410	<0 26	0 82	72	<0 018	0 185	38 5	<2 3	110	42,000
Tissue lipid content (%)	0.1	0 8	1 6	0 2	1 8	4 0						
Sediment organic carbon (%)										0 1	1 3	5 4

[a] n = number of samples analyzed Each sample was composed of three to five individuals
[b] Max = maximum, Min = minimum, TCDD = tetrachlorodibenzo-*p*-dioxin, PeCDD = pentachlorodibenzo-*p*-dioxin, HxCDD = hexachlorodibenzo-*p*-dioxin, HpCDD = heptachlorodibenzo-*p*-dioxin, OCDD = octachlorodibenzo-*p*-dioxin, TCDF = tetrachlorodibenzofuran, PeCDF = pentachlorodibenzofuran; HxCDF = hexachlorodibenzofuran, HpCDF = heptachlorodibenzofuran, OCDF = octachlorodibenzofuran

than 40 measured values above the analytical detection limit in each of the tissue, sediment, and dissolved phases· TCDD, 1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin, 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin, octachlorodibenzo-*p*-dioxin (OCDD), 2,3,7,8-tetrachlorodibenzofuran (TCDF), 2,3,4,7,8,-pentachlorodibenzofuran, and octachlorodibenzofuran (OCDF).

Structural equation modeling with maximum likelihood estimation was performed using AMOS 6 0 software (SPSS). The relative quality of model fit was judged by the chi-square statistic relative to the degrees of freedom, the squared multiple correlation between the dependent variable and the independent predictors, the root-mean square error of approximation, and the Akaike Information Criteria [30] Except as otherwise noted, explanatory variables were retained in the model only if their regression weight was significantly different from zero with 95% confidence Similarly, covariance among explanatory variables was generally retained in a model only if it was statistically significant ($\alpha < 0\ 05$). Structural equation models were rejected if they could be statistically rejected at $\alpha < 0\ 05$ based on the chi-square statistic and degrees of freedom Other statistical analyses were performed using SPLUS software (Insightful)

RESULTS AND DISCUSSION

Concentrations of the 2,3,7,8-substituted PCDD/Fs in HH fillets ranged from less than 0 03 to 72 ng/kg and from less than 0.07 to 410 ng/kg in BC tissue (Table 1) Levels of the tetra-chlorinated congeners TCDD and TCDF were typically among the highest of the PCDD/F congeners in tissues However, tissue concentrations of OCDD and OCDF often exceeded the levels of TCDD and TCDF The median lipid content of BC and HH tissues was 0 8 and 1.4%, respectively.

Levels of TCDD and TCDF in HH and BC tissue appeared to be related to concentrations in sediment organic carbon and water sampled from the same site, implying that the tissues were at least partially in equilibrium with the levels in sediment and water. However, concentrations of the more chlorinated PCDD/F congeners in tissue were only weakly related to levels in sediment and water, if at all

Tissue concentrations were significantly related to lipid levels in most cases, but the relationship was usually weaker than expected from thermodynamics-based EqP theory. This was particularly true for the more chlorinated congeners and for BC The routine practice of lipid normalization for calculating bioaccumulation has been found by others studying animals with low lipid content to be inappropriate [31]. Stowe et al [32] observed that lipids were only a modest predictor of polychlorinated biphenyl concentrations in Lake Michigan salmonids at the individual organism level, and Bonn [33] observed that lipid and sediment organic carbon normalizations did not reduce variance in PCDD/F fish tissue–sediment relationships.

Median lipid-normalized baseline log BAFs ranged from 4 41 to 6 68 L/kg in HH and from 4 91 to 7 03 L/kg in BCs (Fig 1) Median log BSAFs ranged from −3 19 to −0 41 in HH and from −2 57 to −0.24 in BCs (Fig 2) With the exception of TCDF and possibly 1,2,3,7,8,9-hexachlorodibenzofuran, the magnitude and congener patterns of bioaccumulation in BCs were similar to those for HH, likely an indication of the importance of chemical properties in controlling bioaccumulation However, bioaccumulation of TCDF was substantially lower in HH than in BCs, and this pattern was even more accentuated with lipid normalization A substantially reduced bioaccumulation of TCDF, relative to that of TCDD and other PCDF congeners, was also noted by Sijm et al. [34] in goldfish. They calculated a half-life for TCDF of 3 1 d in control fish but more than 7 d in fish exposed to an inhibitor of PCDD/F biotransformation, implying that biotransformation of TCDF is responsible for the reduced bioaccumulation. Loonen et al [35] also noted rapid elimination of TCDF from guppies, with a half-life of 2.4 d compared

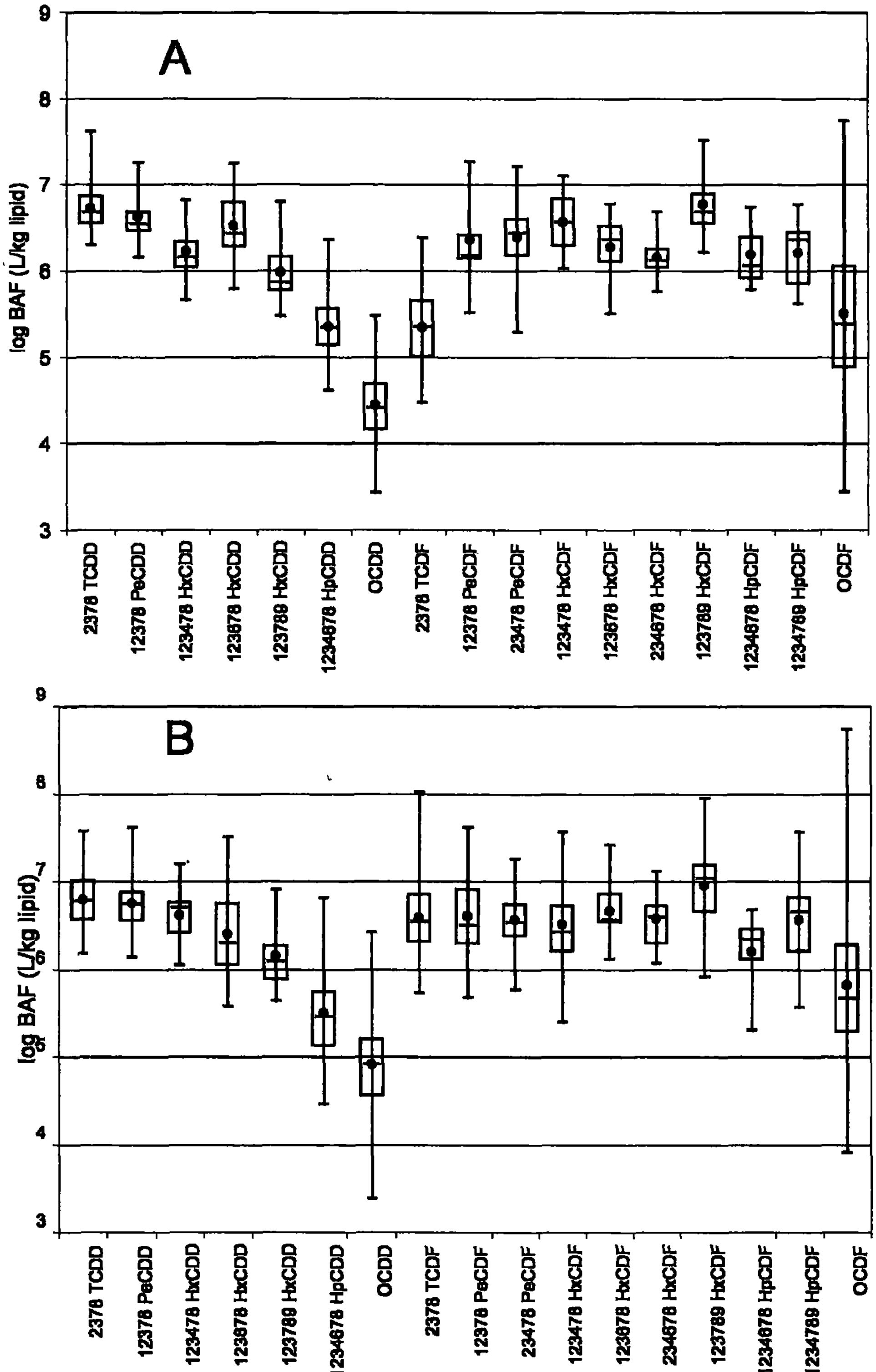

Fig 1 Bioaccumulation factors (BAFs) of polychlorinated dibenzo-*p*-dioxin and dibenzofuran congeners in hardhead catfish (A) and blue crab (B) The first and third quartiles are represented by the vertical extent of each box, the mean by a black dot, the median by a horizontal line inside each box, and the minimum and maximum by the extent of the vertical lines extending above and below each box Congener names are abbreviated for tetrachlorodibenzo-*p*-dioxin (TCDD), pentachlorodibenzo-*p*-dioxin (PeCDD), hexachlorodibenzo-*p*-dioxin (HxCDD), heptachlorodibenzo-*p*-dioxin (HpCDD), octachlorodibenzo-*p*-dioxin (OCDD), tetrachlorodibenzofuran (TCDF), pentachlorodibenzofuran (PeCDF), hexachlorodibenzofuran (HxCDF), heptachlorodibenzofuran (HpCDF), and octachlorodibenzofuran (OCDF)

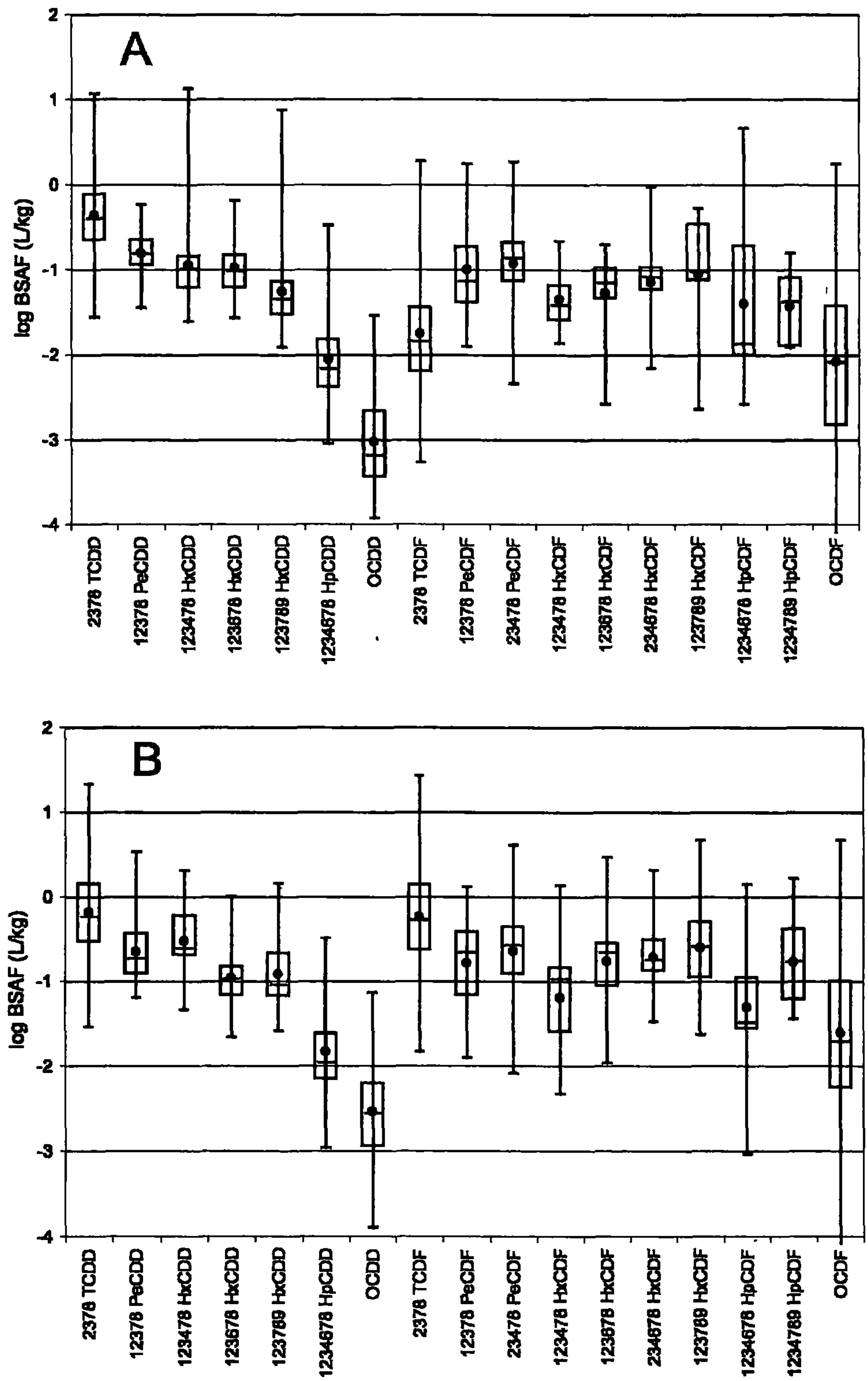

Fig 2 Biota–sediment accumulation factors (BSAFs) of polychlorinated dibenzo-*p*-dioxin and dibenzofuran congeners in hardhead catfish (A) and blue crab (B) Congener names are abbreviated for tetrachlorodibenzo-*p*-dioxin (TCDD), pentachlorodibenzo-*p*-dioxin (PeCDD), hexachlorodibenzo-*p*-dioxin (HxCDD), heptachlorodibenzo-*p*-dioxin (HpCDD), octachlorodibenzo-*p*-dioxin (OCDD), tetrachlorodibenzofuran (TCDF), pentachlorodibenzofuran (PeCDF), hexachlorodibenzofuran (HxCDF), heptachlorodibenzofuran (HpCDF), and octachlorodibenzofuran (OCDF)

to 14 d for TCDD. Bignert et al. [36] noted large spatial differences in the bioaccumulation of TCDF, relative to other congeners, by herring in Bothnian Bay.

For the PCDD congeners, a systematic decline in BAF and BSAF with increasing degree of chlorination, molecular size, and octanol–water partition coefficient (Fig. 3A) was noted, as has been reported by previous investigators [17,37] This pattern is consistent with the hypothesis that permeation of cell membranes is sterically limited for larger PCDDs [11–13,20] Low dietary uptake efficiency [14–15,38] may also limit

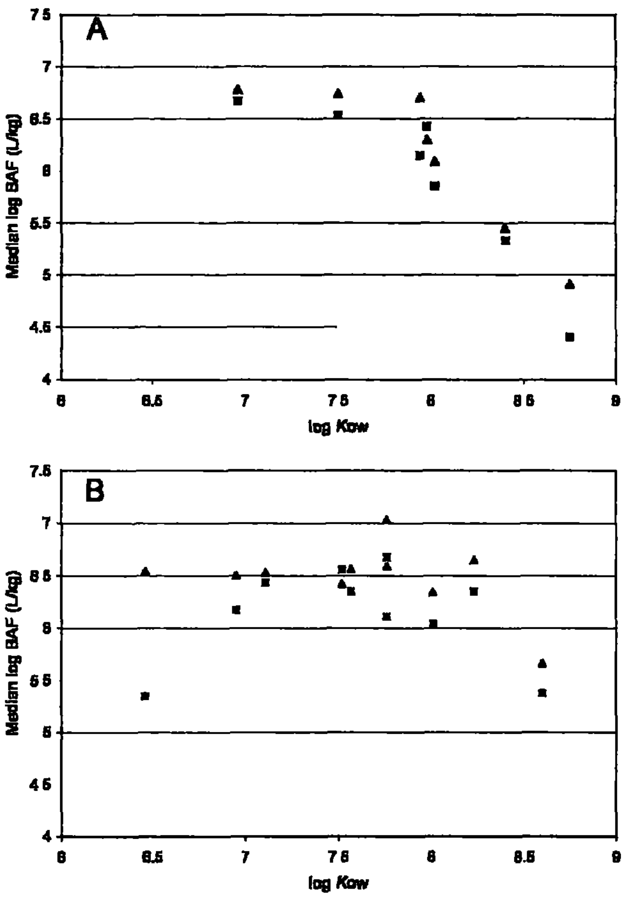

Fig. 3. Relationships between bioaccumulation factors (BAFs) of polychlorinated dibenzo-*p*-dioxins (A) and polychlorinated dibenzofurans (B) and their octanol–water partition coefficients (K_{OW}) in hardhead catfish (■) and blue crabs (▲). Values of K_{OW} are from Govers and Krop [40].

uptake of these high molecular weight congeners. Finally, given that the more chlorinated congeners also tend to be less water soluble and more prone to being strongly sorbed to sediments, alternative hypotheses involving reduced bioavailability [10] may also explain the observations.

The pattern of declining bioaccumulation with degree of chlorination was not evident to the same extent for PCDF congeners (Fig. 3B). In fact, the average BAFs and BSAFs for TCDF in HH were among the lowest of any PCDD/F congener. The absence of an observed reduction in bioaccumulation with increasing molecular size for the PCDF congeners (except for OCDF), and the apparent reduction in bioaccumulation for TCDF in HH relative to BCs, appears more consistent with a hypothesis that metabolism limits bioaccumulation of PCDFs. Burkhard et al. [10] have shown that metabolism and reduced assimilation efficiencies of PCDD/Fs reduce their BSAFs in lake trout by up to four orders of magnitude below those of relatively unmetabolizable polychlorinated biphenyls of comparable hydrophobicity. However, it should be noted that some other studies [17,37] have observed a systematic reduction in bioaccumulation with molecular size for the PCDFs congeners.

At less contaminated sites, observed BAFs and BSAFs were typically higher than those from sites where PCDD/F concentrations were higher (as illustrated in Fig. 4 for TCDD). This has been observed elsewhere [39] and may be explained as

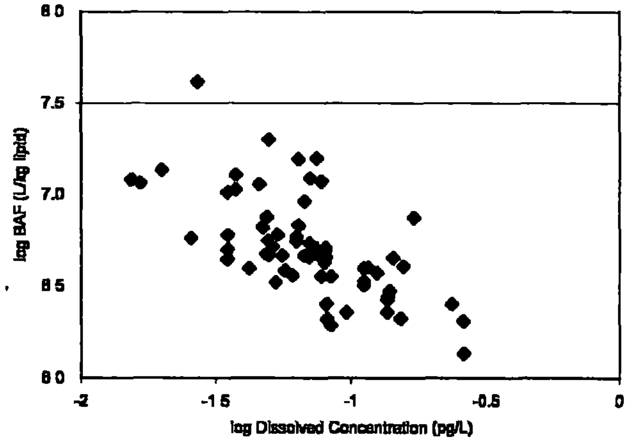

Fig. 4. Relationship between bioaccumulation factors (BAFs) in hardhead catfish and dissolved concentrations for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin.

follows: HH, BCs, and some of their prey are mobile organisms, and water concentrations are dynamic, so they are exposed to PCDD/F levels from more and less contaminated sites that do not represent only the site and time where they are collected. Thus, it is important to evaluate the risks of contaminant bioaccumulation in light of the temporal and spatial variability of exposure, as well as the mobility and life history of the species.

Structural equation modeling

Hardhead sea catfish. Figure 5A shows a rather complex network of factors affecting the levels of TCDD in HH tissue. This SEM explained 62% of the variance in measured concentrations, with the balance attributed to other factors not in the model (including measurement error). The tissue concentration showed a strong positive association with lipid content, with a standardized regression coefficient of 0.47. A strong association was also seen between tissue and sediment TCDD concentrations (standardized regression coefficient = 0.35). Sediment concentrations exerted more than twice as much influence on tissue concentrations as did dissolved concentrations (standardized regression coefficient = 0.15). As expected, strong covariation (0.63) occurred between sediment and dissolved concentrations. Other statistically significant factors related to tissue levels were the site depth and the Julian day number of the year. The relationship with depth primarily reflected that TCDD tissue levels of HH collected in the deep channels tended to be higher than those collected in the bays, even after accounting for the covariation between dissolved concentrations and depth (no significant independent covariation occurred between depth and sediment concentration). The covariance between dissolved TCDD concentrations and site depth likely reflected that many of the shallower Galveston Bay sites were less contaminated than those in the more confined HSC upstream. A weak but statistically significant relationship between TCDD concentrations in tissue and Julian day number was observed, which implied that tissue TCDD levels declined as the year progressed. Given that HH are known to migrate from the HSC system to presumably less contaminated waters over the winter, this result is counterintuitive. The possibility that this observation could be explained by autumn recruitment of less-contaminated juveniles into the size ranges collected was considered. However, fish length and

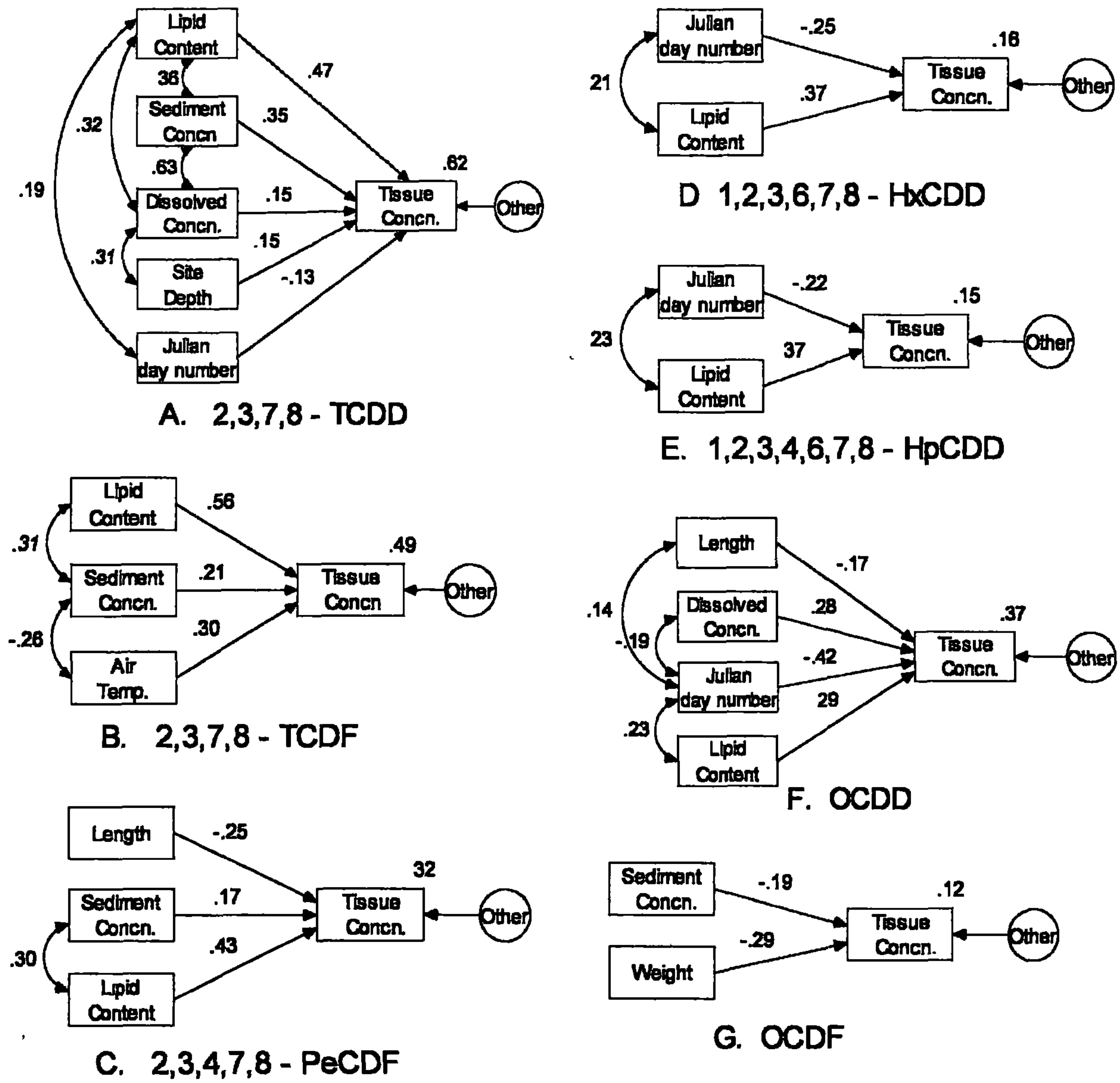

Fig. 5. Structural equation models of bioaccumulation of selected polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F) congeners in hardhead catfish fillets (tissue) Double-headed arrows represent standardized covariances Single-headed arrows represent standardized model regression weights The squared multiple correlation (just above and to the right of the tissue box) is the fraction of the variance in tissue concentrations explained by the model (A) 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), (B) 2,3,7,8-tetrachlorodibenzofuran (TCDF); (C) 2,3,4,7,8-pentachlorodibenzofuran (PeCDF), (D) 1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin (HxCDD); (E) 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (HpCDD), (F) octachlorodibenzo-*p*-dioxin (OCDD), (G) octachlorodibenzofuran (OCDF)

lipid content were positively related to Julian day number, indicating that HH became longer and fatter over the course of the year. Thus, it may be that the association between tissue concentration and day number resulted from growth dilution [22] or a shift to less contaminated prey. Note that lipid levels covaried with sediment and dissolved concentrations, which seems to indicate that fatter fish live in the more contaminated areas, which are also probably in the more productive, less salty waters

It is important to note that while other explanatory variables do not appear in the SEM, this indicates not a lack of covariance with tissue concentrations but rather a covariation with the tissue concentrations that was not statistically significant after accounting for their covariation with other independent predictors in the model. Thus, it was rare for more than one strongly covarying factor (e.g., day number and air temperature or length and weight) to show up as significant in the SEM.

The SEM illustrated in Figure 5B explained 49% of the variability in TCDF concentrations in HH Lipid content appeared to exert the greatest influence on observed variations in tissue levels Other significant relationships were observed with sediment concentrations and air temperature, an indicator of seasonality

The SEM for 2,3,4,7,8-pentachlorodibenzofuran in HH (Fig. 5C) explained only 32% of observed variability in tissue concentrations. As with TCDD and TCDF, lipid content and sediment concentrations were significant predictors of levels in tissue. The SEM also indicated that organism size in HH, as indicated by length, was inversely related to tissue levels.

The SEMs for 1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin (Fig. 5D) and 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (Fig. 5E)

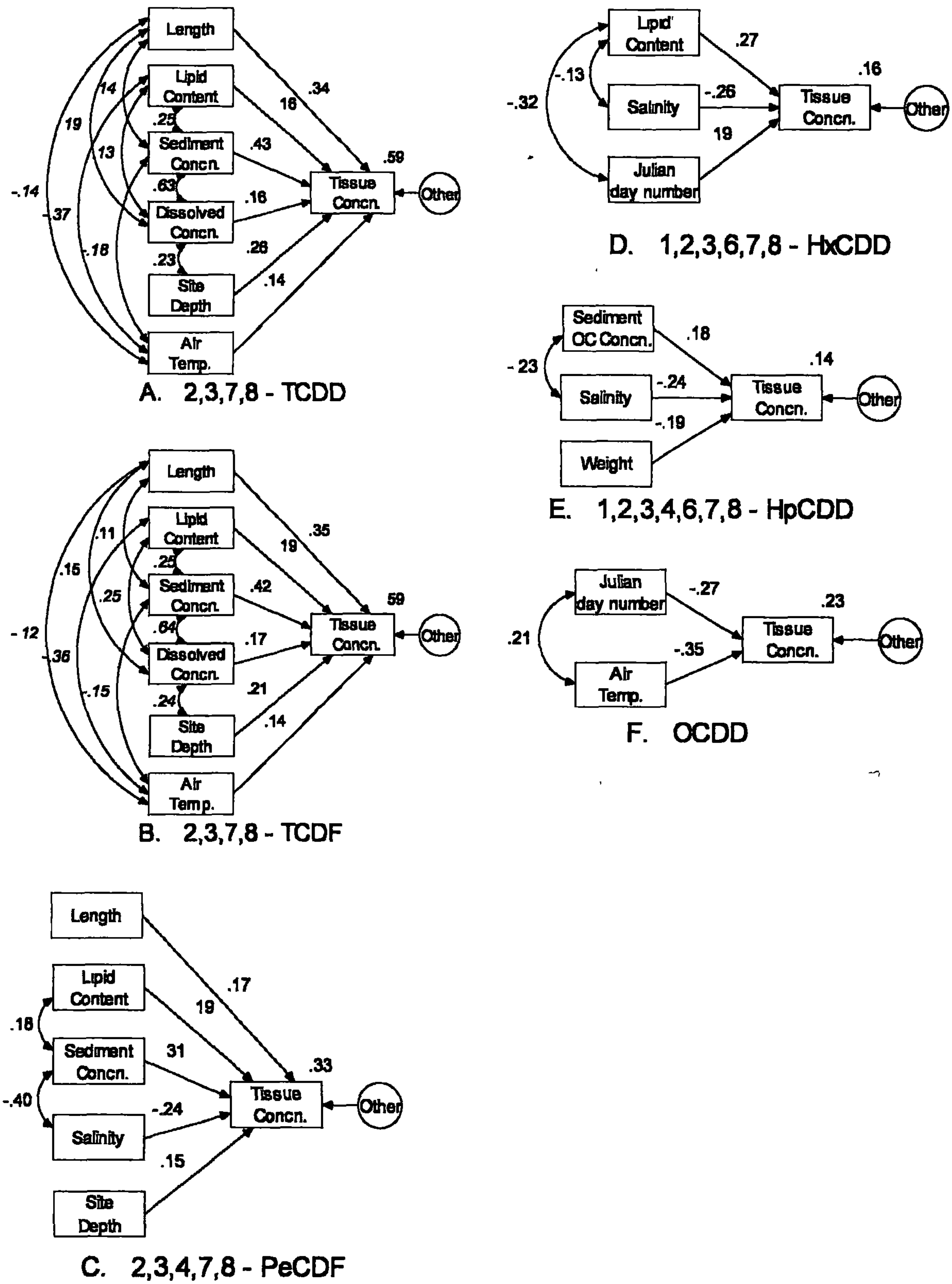

Fig 6 Structural equation models of bioaccumulation of selected polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F) congeners in blue crab tissue Double-headed arrows represent standardized covariances Single-headed arrows represent standardized model regression weights The squared multiple correlation (just above and to the right of the tissue box) is the fraction of the variance in tissue concentrations explained by the model (A) 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD); (B) 2,3,7,8-tetrachlorodibenzofuran (TCDF), (C) 2,3,4,7,8-pentachlorodibenzofuran (PeCDF), (D) 1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin (HxCDD), (E) 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (HpCDD), (F) octachlorodibenzo-*p*-dioxin (OCDD).

in HH were simple and explained less than 20% of the variance in the tissue concentrations. Only lipid content and Julian day number were significantly related to HH tissue concentrations. The limited ability of these SEMs to explain variations in tissue concentrations of pentachlorodibenzofuran indicates that other factors, such as metabolism, controlled the levels in tissues.

The SEM for OCDD (Fig. 5F) explained 37% of the observed variance in tissue concentrations in HH. As with all other PCDDs in HH, lipid content and day number were significantly related to tissue concentrations Day number was the strongest predictor of tissue concentrations, with a standardized regression coefficient of −0 42. The dissolved OCDD concentration, but not the concentration in sediment, was also significantly related to tissue concentration in this model. Finally, fish length was inversely related to tissue concentration, which may provide some support for the hypothesized impact of growth dilution or a shift to less contaminated prey species

The SEM for OCDF in HH (Fig. 5G) explained only 12% of the variability in observed tissue concentrations. In addition to sediment concentrations, fish weight was a significant (inverse) predictor of tissue concentrations.

Blue crab The SEM for TCDD in BCs (Fig 6A) explained 59% of the variability in observed tissue concentrations. As seen in HH, both sediment and dissolved phase TCDD concentrations were significantly related to tissue concentrations, with sediments exhibiting the much stronger relationship by a factor greater than two. Also similar to HH, BC tissue concentrations were significantly related to the total water depth at the sampling site and lipid content. In contrast to HH, tissue concentrations of TCDD in BC were only weakly related to lipid content. The length or, more accurately, width of the BC carapace was significantly related to tissue levels, with larger BC having higher levels of TCDD

The SEM for TCDF in BC also explained 59% of the variability in tissue concentrations (Fig 6B). This SEM exhibited pronounced similarity to that for TCDD, implying that the processes controlling bioaccumulation are similar However, note that this SEM for BC was very different from that for HH. The SEM for 2,3,4,7,8-pentachlorodibenzofuran in BC (Fig 6C) was also similar to those for TCDD and TCDF but explained only 33% of the variance in tissue concentrations. Air temperature and dissolved phase concentrations were not significant predictors of tissue concentrations, but salinity emerged as a significant inverse predictor

The SEMs for 1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin and 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin in BC tissue (Fig 6D and E) account for less than 20% of the observed variance in tissue concentrations Salinity was expected to be inversely related to tissue concentrations because the most contaminated areas were in less saline waters. Alternatively, the inverse relationship with salinity may reflect the inclusion of female crabs in the higher-salinity waters. Female crabs are reported to spend part of the year spawning in the Gulf of Mexico [24] and thus would be less exposed to PCDD/F contamination. However, these relationships explained little of the variance in tissue concentrations

The SEMs for OCDD in BC (Fig 6F) explained only 23% of the variability in tissue concentrations, only two seasonal effects, air temperature and day number, exhibited statistically significant relationships with tissue concentrations No predictor variables exhibited statistically significant relationships with OCDF levels in BC tissues

CONCLUSIONS

As predicted by EqP theory, the important influences of chemical properties, chemical concentrations in water and sediment, and tissue lipid content were apparent in the bioaccumulation of PCDD/F congeners in HH and BC of the HSC system However, a large percentage of the variation in bioaccumulation could not be explained by EqP theory, indicating the great complexity of the system This was particularly true for the penta- to octa-chlorinated congeners. Bioaccumulation factors and BSAFs declined with degree of chlorination for PCDD congeners, which may reflect steric constraints on membrane permeation, low dietary uptake efficiency, or reduced bioavailability due to strong sorption to bed and suspended sediment and colloidal phases. An apparent reduction in BAFs and BSAFs with increased concentrations in the sediment and water phases may be explained by the variable exposure of mobile organisms along wide-ranging spatial and temporal gradients of chemical contamination.

For both BC and HH, tissue concentrations appeared to be related more closely to sediment than water concentrations This implies that sediments are the more important route of exposure for PCDD/Fs Remediation efforts focused on legacy sediment contamination may be most effective in reducing tissue burdens of PCDD/Fs

Other factors also apparently affect the extent of bioaccumulation in this system. These may include seasonal factors related to the organisms' temperature preferences and reproductive behavior, seasonal recruitment, the mobility of the organisms together with spatially heterogeneous concentrations in sediment and water, and the size and age of individual organisms. It is important to evaluate the risks of contaminant bioaccumulation in light of the temporal and spatial variability of exposure, as well as the mobility and life history of the species After considering known variables, a large pool of unexplained variance existed in the levels of bioaccumulation, particularly for the more chlorinated congeners Some of this variation may be explained by analytical uncertainty; however, biotransformation may also be an important factor in controlling the levels of bioaccumulation.

Acknowledgement—Funding for the present study was provided by the Texas Commission on Environmental Quality and the U S EPA The authors acknowledge both agencies for their support, however, the views expressed in this manuscript are strictly their own and do not reflect agency review or approval The authors thank two anonymous reviewers

REFERENCES

1 Suarez MP, Rifai HS, Palachek RP, Dean KE, Koenig L 2006 Distribution of poly-chlorinated dibenzo-*p*-dioxins and dibenzofurans in suspended sediments, dissolved phase, and bottom sediment in the Houston Ship Channel *Chemosphere* 62 417–429
2 Suarez MP, Rifai HS, Palachek RP, Dean KE, Koenig L 2005 Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in Houston Ship Channel tissue and sediment. *Environ Engineer Sci* 22 891–906
3 Di Toro DM, Zarba CS, Hansen DJ, Berry WJ, Swartz RC, Cowan CE, Pavlou SP, Allen HE, Thomas NA, Paquin PR 1991 Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning *Environ Toxicol Chem* 10 1541–1583
4 Mackay D 1979 Finding fugacity feasible *Environ Sci Technol* 13 1218–1223
5 Karickhoff S 1981 Semi-empirical estimation of sorption of hydrophobic pollutants in natural sediments and soils *Chemosphere* 8 833–846.

6 Persson NJ, Gustafsson O, Bucheli TD, Ishaq R, Naes K, Broman D 2002. Soot–carbon influenced distribution of PCDD/F in the marine environment of the Grenlandsfjords, Norway *Environ Sci Technol* 36 4968–4974

7 Clayton JR, Pavlou SP, Breitner NF 1977 Polychlorinated biphenyls in coastal marine zooplankton Bioaccumulation by equilibrium partitioning *Environ Sci Technol* 11 676–682

8 Servos MR, Muir DCG, Webster GRB. 1989 The effect of dissolved organic matter on the bioavailability of polychlorinated dibenzo-*p*-dioxins *Aquatic Toxicol* 14 169–184

9. U S Environmental Protection Agency 2003 Methodology for deriving ambient water quality criteria for the protection of human health—2000, Vol 2—Development of National Bioaccumulation Factors EPA 822/R03/030 Technical Support Document Office of Water, Washington, DC

10 Burkhard LP, Cook PM, Lukasewycz MT 2004 Biota–sediment accumulation factors for polychlorinated biphenyls, dibenzo-*p*-dioxins, and dibenzofurans in southern Lake Michigan lake trout (*Salvelinus namaycush*) *Environ Sci Technol* 38 5297–5305

11 Lyytikäinen MP, Hirva P, Minkkinen P, Hämalainen H, Rantalainen A-L, Mikkelson P, Paasivirta J, Kukkonen JVK 2003. Bioavailability of sediment-associated PCDD/Fs and PCDEs Relative importance of contaminant and sediment characteristics and biological factors *Environ Sci Technol* 37· 3926–3934

12 Muir DCG, Marshall WK, Webster GRB 1985 Bioconcentration of PCDDs by fish. Effect of molecular structure and water chemistry. *Chemosphere* 14 829–833

13 Opperhuizen A, Velde EW, Gobas FAPC, Liem DAK, Steen JMD, Hutzinger O 1985 Relationship between bioconcentration in fish and steric factors of hydrophobic chemicals *Chemosphere* 14 1871–1896

14 Niimi AJ, Oliver BG 1986 Biological half-lives of chlorinated dibenzo-*p*-dioxins and dibenzofurans in rainbow trout (*Salmo gairdneri*) *Environ Toxicol Chem* 5 49–53

15 Opperhuizen A, Sijm D. 1990 Bioaccumulation and biotransformation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in fish *Environ Toxicol Chem* 9 175–186

16 Wong CS, Capel PD, Nowell LH 2001 National-scale, field-based evaluation of the biota–sediment accumulation factor model *Environ Sci Technol* 35 1709–1715

17. Naito W, Jin J, Kang Y-S, Yamamuro M, Masunaga S, Nakanishi J 2003 Dynamics of PCDDs/DFs and coplanar PCBs in an aquatic food chain of Tokyo Bay *Chemosphere* 53 347–362

18 Stange K, Swackhamer DL 1994 Factors affecting phytoplankton species–specific differences in accumulation of 40 polychlorinated biphenyls (PCBs) *Environ Toxicol Chem* 13 1849–1860

19. Cornelissen G, Gustafsson O 2005 Prediction of large variation in biota to sediment accumulation factors due to concentration-dependent black carbon adsorption of planar hydrophobic organic compounds *Environ Toxicol Chem* 24 495–498

20. Jabusch TW, Swackhamer DL 2004 Subcellular accumulation of polychlorinated biphenyls in the green alga *Chlamydomonas reinhardtii. Environ Toxicol Chem* 23 2823–2830

21 Gobas FAPC, Clark KE, Shiu WY, Mackay D 1989 Bioconcentration of polybrominated benzenes and biphenyls and related superhydrophobic chemicals in fish Role of bioavailability and elimination into the feces *Environ Toxicol Chem* 8 231–245

22 Herendeen RA, Hill WA 2004 Growth dilution in multi-level food chains *Ecol Mod* 178:349–356

23 Sheridan PF, Trimm DL 1983 Summer foods of Texas coastal fishes relative to age and habitat *Fishery Bulletin* 81 643–647

24 Perry HM, McIlwain TD 1986 Species profiles Life histories and environmental requirements of coastal fishes and invertebrates (Gulf of Mexico)—Blue crab U S Fish and Wildlife Service Biological Report 82 (11 55). U S Army Corps of Engineers, Vicksburg, MS

25 Muncy RJ, Wingo WM 1983 Species profiles· Life histories and environmental requirements of coastal invertebrates (Gulf of Mexico)—Sea catfish and gafftopsail U S Fish and Wildlife Service Biological Report 82 (11 5). U S Army Corps of Engineers, Vicksburg, MS

26. McElyea B 2003 An evaluation of nekton at two cooling water intake systems in the HSC from 1972 to 2001 AS-190. Texas Commission on Environmental Quality, Austin, TX, USA.

27 Thomas JL, Zimmerman RJ, Minello TJ 1990 Abundance patterns of juvenile blue crabs (*Callinectes sapidus*) in nursery habitats of two Texas bays *Bull Mar Sci* 46 115–125

28 Landrum PF, Nihart SR, Eadie BJ, Gardner WS 1984 Reverse-phase separation method for determining pollutant binding to Aldrich humic acid and dissolved organic carbon of natural waters *Environ Sci Technol* 18 187–192

29 Arhonditsis GB, Stow CA, Steinberg LJ, Kenney MA, Lathrop RC, McBride SJ, Reckhow KH 2006 Exploring ecological patterns with structural equation modeling and Bayesian analysis. *Ecol Model* 192 385–409

30 Akaike H 1987 Factor analysis and AIC *Psychometrika* 52 317–332

31 Bergen BJ, Nelson WG, Quinn JG, Jayaraman S. 2000 Relationships among total lipid, lipid classes, and polychlorinated biphenyl concentrations in two indigenous populations of ribbed mussels (*Geukensia demissa*) over an annual cycle *Environ Toxicol Chem* 20:575–581

32 Stowe CA, Jackson LJ, Amrhein JF 1997 An examination of the PCB·lipid relationship among individual fish *Can J Fish Aquat Sci* 54 1031–1038

33 Bonn BA 1998 Polychlorinated dibenzo-*p*-dioxin and dibenzofuran concentration profiles in sediment and fish tissue of the Willamette Basin, Oregon *Environ Sci Technol* 32 729–735

34 Sijm DTHM, Wever H, Opperhuizen A 1993 Congener-specific biotransformation and bioaccumulation of PCDDs and PCDFs from fly ash in fish *Environ Toxicol Chem* 12 1895–1907

35 Loonen H, Tonkes M, Parsons JR, Govers HAJ 1994 Bioconcentration of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in guppies after aqueous exposure to a complex PCDD/PCDF mixture. Relationship with molecular structure *Aquat Toxicol* 30 153–169

36 Bignert A, Nyberg E, Sundqvist KL, Wiberg K 2007 Spatial variation in concentrations and patterns of the PCDD/F and dioxin-like PCB content in herring from the northern Baltic Sea *J Environ Monit* 9 550–556

37 Yunker MB, Cretney WJ 2000 Bioavailability of chlorinated dibenzo-*p*-dioxins and dibenzofurans to Dungeness crab (*Cancer magister*) at marine pulp mill sites in British Columbia, Canada *Environ Toxicol Chem* 19 2997–3011

38 Gobas FAPC, Muir DCG, Mackay D 1988 Dynamics of dietary bioaccumulation and faecal elimination of hydrophobic organic chemicals in fish. *Chemosphere* 17:943–962

39. Cretney WJ, Yunker MB 2000 Concentration dependency of biota–sediment accumulation factors for chlorinated dibenzo-*p*-dioxins and dibenzofurans in Dungeness crab (*Cancer magister*) at marine pulp mill sites in British Columbia, Canada *Environ Toxicol Chem* 19 3012–3023

40. Govers HAJ, Krop HB 1998 Partition constants of chlorinated dibenzofurans and dibenzo-*p*-dioxins *Chemosphere* 37 2139–2152